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THERMODYNAMICS

by LESTER C. LICHTY

Professor of Mechanical Engineering
Yale University

SECOND EDITION

NEW YORK AND LONDON
McGRAW-HILL BOOK COMPANY, INC.
1948

THERMODYNAMICS

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PREFACE TO THE SECOND EDITION

Experience with the first edition proved that the grouping of the subject matter simplified the process of developing the student's analytical ability. Consequently, the same general arrangement of material has been retained while much of the text has been rewritten to clarify the more difficult parts. The old chapter on Properties of Mediums and Processes has been divided into two chapters and a section on nonsteady-flow processes has been added. Also, a section on gas turbines is now included in the chapter on Internal-combustion-engine and Gas-turbine Processes since the methods of analysis are identical.

The Energy Equation and its application have been simplified by elimination of the delta form (differences of entering or leaving, etc., forms of energy). A further simplification is made by assuming that all forms of energy are positive in sign, thus eliminating the necessity of observing mathematical conventions regarding signs when integrating expressions for work or heat-transfer areas.

The idea of an imaginary envelope surrounding the apparatus or mediums focuses the student's attention on the forms of energy involved in the various processes. In all cases the analysis goes back to the Energy Equation for the process rather than to some equation or relation already developed.

Tables of values of $\int c_v dT/T$ and $\int c_p dT/T$ for gases have been added and new values for internal energy replace the old values, this revision practically eliminating the need for specific-heat equations in the evaluation of internal energy and entropy of gases. No longer is it necessary or desirable to use PV^k = constant for solving adiabatic-isentropic processes since they may be solved with these tables accurately and quickly.

Deviation from perfect-gas conditions is introduced in the chapter on Properties of Mediums by the use of the residual volume v and the compressibility factor Z in $PV = ZRT$. Illustrative examples dealing with deviations in enthalpy and entropy with pressure are included in the appendix.

The chapter on Availability of Energy has been appreciably amplified and clarified. The treatment of combustion processes is a revision of that which appeared in the author's latest edition of Internal Combustion Engines. A new combustion chart for gas-turbine processes is included.

The chapter on Flow of Fluids includes material dealing with supersonic flow, Mach number, shock, jet and rocket propulsion, and the Moody friction chart. The section on flow over blades now deals with compressor as well as turbine blades. Ram-chamber and diffuser processes are included.

More diagrammatic sketches of apparatus arrangement as well as illustrative examples have been introduced throughout the book. As many more exercises are included at the end of each chapter, not all of them can be solved in the time allotted for the usual course. Consequently, some of the more difficult ones should be omitted in order to give the student some experience with and appreciation of all the major subdivisions of the subject. Some of the exercises indicate the type of original questions or problems that may be formulated for quiz purposes.

More data on properties of mediums are tabulated in the appendix, including some on Freon-12, compressibility factors, and reaction data.

The symbol U is used for internal energy, and deg Rankine (°R) for deg F abs. The use of the negative exponent for dimensions (lb in.$^{-2}$) has been abandoned in favor of the fraction sign (lb/in.^{2}). The symbol lb/in.^{2} is used in preference to psia in order to make the student more dimension conscious.

Thus, the revision is practically a rewritten book retaining that which has been found satisfactory, discarding that which is obsolete or unsatisfactory, and adding that which simplifies, improves, or extends the understanding of thermodynamics and its application to engineering processes.

The author is indebted to his colleagues D. R. Olson, B. R. Onuf, C. W. Phelps, and P. J. Waibler, to visiting professors A. D. Lewis, B. H. Spurlock, and E. H. Stolworthy, and to G. H. Van Hengel for the many suggestions resulting from their experience with the teaching of much of the material contained herein, and to Henry Margenau, professor of physics, Yale University, for reviewing the chapter on Availability of Energy and for providing the material in the appendix dealing with the viewpoint of modern physics regarding the Characteristic Equation.

LESTER C. LICHTY

NEW HAVEN, CONN.
January, 1948

PREFACE TO THE FIRST EDITION

The subject of thermodynamics has so baffled the average student that it has acquired the undesirable reputation of being a most formidable subject in which only the gifted can understand and satisfy more than the minimum requirements. This reputation has been fostered, perhaps unconsciously, by the efforts of many teachers and writers of texts on this subject, who have introduced the ramifications that have mystified and led the student away from fundamental thinking. This text is an attempt to simplify the treatment, to strip it of many of the mathematical manipulations for which there is no excuse except to obtain an equation into which data can be substituted without fundamental analysis, and to consolidate the treatment into logical groupings from a standpoint of thermodynamic analysis rather than mechanical equipment. It is also an attempt to establish a better balance between vapor and combustion processes, since the latter usually are neglected.

All of the energy terms are introduced in the beginning so that throughout the text the student should analyze each process with regard to all the various forms of energy. Two of the three energy terms obtained by integration are set up to satisfy mathematical conventions. Thus,

$$\Delta W = \text{Work}_{\text{out}} - \text{Work}_{\text{in}} = \int_{V_1}^{V_2} PdV$$

which will be positive and indicate Work_{out} when V_2 is greater than V_1, and vice versa. Also, depending upon the state of the medium,

$$\Delta E = E_2 - E_1 = \int_{T_1}^{T_2} f(T)$$

which will be positive and indicate an increase in Internal Energy when T_2 is greater than T_1, and vice versa.

With the foregoing convention,

$$\Delta Q = \text{Heat}_{\text{out}} - \text{Heat}_{\text{in}} = -\int_{S_1}^{S_2} TdS$$

for the reversible process, which will be negative and indicate Heat_{in} when S_2 is greater than S_1, and vice versa.

The properties of vapors and gases are developed in the same chapter, dealing first with one state and then the other in the same section, showing the underlying principles to be the same, and developing a comprehensive attitude regarding the state of a medium. Some problems range from one state of a medium into another and necessitate the use of data for both the vapor and gaseous states, as well as a consideration of the different bases for the properties of the two states. The student should be taught that there is no fine line of demarcation between these two states, but that they merge gradually, and that the relationships for media in the gaseous state are very unreliable unless the condition of the medium is such that the Enthalpy and Internal Energy are very nearly functions of the temperature only.

The availability of energy is approached from the broad viewpoint of the possibility of transformation of all forms of energy into Mechanical Work, leading up to the Heat-Work availability which is so important in this subject. The effect of Heat transfer and fluid friction is treated extensively in this chapter, the text having dealt with reversible processes only prior to this section.

Both engine and compressor cycles are analyzed by the application of the same principle and, consequently, are treated in one chapter, rather than in separate chapters for different types of mechanical equipment or for different media.

The combustion process is treated primarily from a standpoint of Chemical Energy, which is one of the terms in the Energy Equation. It should be observed that heating value appears in the Energy Equation only upon manipulation, which in some cases is necessary.

The internal-combustion engine process is not a thermodynamic cycle and should never have been treated as such. It is a combustion process dealing with the liberation of Chemical Energy in a mixture of fuel, air, and clearance products, in which variable specific heats and chemical equilibrium are important factors. With the present knowledge of these factors there is little excuse for the air-standard analysis, and no student should leave this subject with the erroneous ideas instilled by the use of only this mythical analysis.

The flow of fluids through orifices and nozzles, over both moving and stationary turbine blades, through turbines, and through pipe lines is logically treated in one chapter dealing with flow.

Throughout the text, the analysis leads to the development of simple fundamental relationships, which are not combined or manipulated in most cases to the point where they lose their significance and become merely formulas into which data can be substituted and a result obtained. No symbol for the conversion of energy units appears in any of the equations, it being understood that there is no equation unless the dimensions of all terms of an equation are the same. Thus the student is put upon his own responsibility to substitute only those terms which will make the equation dimensionally consistent. There are those who view, the expression $\int PdV$ as being only pressure times volume change and therefore as having only the dimension of foot-pounds. However, the broader viewpoint is that it is an expression for Work which may be evaluated in any desired dimensions.

While all the foregoing has been done with the objects of simplifying the treatment, of staying closer to fundamental reasoning, of making the student dimension conscious, and of forcing him to think, the teacher of this subject should do his part with original propositions, questions, and examinations which require the student to analyze and apply the comparatively few and simple principles underlying this subject rather than substitute values and compute results.

The development of the classical relations between the coordinates and properties of media are located in the Appendix. There are some who would prefer to consider this subject either before or immediately after the chapter dealing with properties of media. The author prefers to treat this subject after the study of the text. However, no student should leave a course in thermodynamics without being aware of this phase of the subject.

Tables of data dealing with the properties of various media are also located in the Appendix rather than scattered through the text. Skeleton tables of more complete works are used, but most of the illustrative examples are designed so that the data can be obtained from these tables. Various charts which facilitate computations are also located in the Appendix. These should not be used until after the student has been thoroughly grounded in the properties of media.

The author is very much indebted to the various sources of information from which data have been obtained and for which credit is given at various places in the text.

LESTER C. LICHTY

NEW HAVEN, CONN.
May, 1936

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CHAPTER I

THERMODYNAMIC MEDIUMS AND THEIR COORDINATES

Thermodynamics.—Thermodynamics is a science which deals with the properties of mediums, energy, and energy transformations. It is the basis for the analysis of energy transformations that may occur when a medium undergoes a change from one condition to another in any kind of process. Common processes are those of heating and cooling, the compression of a gas requiring an input of work, the obtaining of work by the expansion of steam in an engine cylinder, etc. Chemical reaction occurs in some processes, and several mediums may be combined into another medium or other mediums, or a medium may be dissociated into other mediums. In both cases energy may be liberated or absorbed by the mediums undergoing the reaction process.

Thermodynamics also indicates the possibility of obtaining work from the various forms of energy, processes, and mediums. Consequently, it is most important to have a clear conception of thermodynamic mediums and their defining coordinates.

Thermodynamic Mediums.—All thermodynamic processes require the use of some medium or mediums. The medium is usually required to absorb or reject energy with or without chemical reaction, to serve as a carrier of the energy (except radiation) to or from some apparatus, and to do work or have work done on it. The properties of a medium should be such that the foregoing or desired processes can be accomplished under the desired conditions.

Some mediums are more desirable than others for a given process. Water is a very desirable medium for the power-generation process, since it readily absorbs heat, flows easily to the engine, and at reasonable temperatures will exert a pressure against an engine piston while it moves and permits considerable expansion of volume. Obviously, iron and wood are not desirable mediums for this process.

For the artificial ice plant ammonia is a desirable medium since it will boil at temperatures below 32 F while at moderate pressures, and absorb heat from water as it freezes into ice. Also, ammonia can be condensed at atmospheric temperatures while under reasonable pressure.

Air and a fuel are required for the internal-combustion engine process, and the reaction of the oxygen in the air with the fuel results in gaseous products of combustion that readily exert a pressure on the engine piston and cause it to move.

Thus, the various states of mediums ranging from solid to gaseous must be dealt with in the study of thermodynamics.

A medium in any state consists of many molecules, about 8×10^{23} per cubic foot of gas at atmospheric conditions. The molecules of a solid are restricted in motion to that of vibration about their mean positions. As the solid melts to a liquid, the molecules are free to move about with a motion of translation. In the vapor and gaseous states molecules are moving at random in all directions.

The Defining Coordinates.—Although a medium consists of a great number of molecules in motion, the description of which requires the use of statistical mechanics, the medium may be described by the effect of a given mass of its molecules on the walls of the confining chamber and on a temperature-measuring device inserted therein. Thus, the state or condition of a unit quantity of medium is defined by its volume, V, pressure, P, and temperature, T. It is customary to consider as a unit quantity of material either that amount which weighs 1 lb, or the molecular weight of the substance (1 *mole*)* in pounds, both at sea level.

A unit quantity of a solid or liquid, at a given pressure and temperature, will have a definite volume. An increase in pressure will decrease the volume slightly, while an increase in temperature usually increases the volume a small amount. A unit quantity of a gas may have various volumes, depending upon pressure and temperature. Experimental evidence has shown that any two of the three coordinates determine the remaining coordinate of a given quantity of the medium. Thus,

$$V = f(P,T), \text{ or } P = f(V,T), \text{ or } T = f(P,V)$$

where f indicates function of or relation between the variables indicated.

Volume.—The volume of a medium is measured in cubic feet (ft^3) in the English system of measurements. For a unit quantity of a medium the measurement becomes cubic feet per pound weight (ft^3/lb) or cubic feet per mole ($ft^3/mole$), which, by definition, is the *specific volume.* The *specific weight* of a medium is the reciprocal of the specific volume and is expressed as pounds weight per cubic foot (lb/ft^3) or moles per cubic foot ($moles/ft^3$).

Pressure.—A solid rests on a base and exerts a force on that base equal to its weight. This force may or may not be distributed uniformly over the entire base. In either case, the mean unit force, or pressure, is equal to the total weight in pounds divided by the base area in square feet and is expressed in pounds per square foot (lb/ft²).

---

* By definition the number of molecules in a mole is the same regardless of the medium.

A liquid exerts a pressure on the base and against the sides of a containing vessel. At any given point in the liquid the pressure is the same in all directions, and the pressure at any point depends on the weight of the liquid above a unit area at that point. Thus, neglecting the compressibility of liquids (see Table V, Appendix) the pressure of a liquid in a tank varies in a straight-line relationship (Fig. 1) from zero pressure at the top of the liquid to a pressure P, at the bottom of the tank, equivalent to the weight of the column of liquid of unit cross section. (This does not include the effect of the atmosphere that exerts a pressure on the surface of the liquid.)

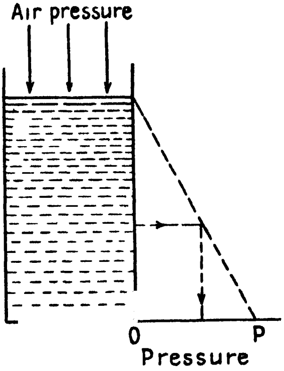

Fig. 1 —Pressure of liquid.

A gas exerts a pressure against all the walls of a containing vessel. The pressure is caused by the bombardment of the walls by the molecules of the gas and is usually assumed to be the same at every point in the gas. However, for gas columns of considerable height or weight, the pressure varies for different positions in elevation, being greater at the bottom than at the top of the container. Also, since gas is readily compressible, the relation between pressure and elevation in a gas column is not a straight line.

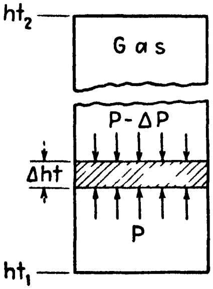

Fig. 2.—Enclosed gas column.

At any given position in a gas column (Fig. 2) assume the pressure to be P. At a slightly higher position the pressure will be $P - \Delta P$, the decrease ΔP being equivalent to the weight of the element Δht high and of unit cross section. Since the weight of any volume of gas is the product of the volume and the specific weight

$$-\Delta P = -\Delta wt = \Delta ht \times \text{specific weight}$$
$$= \Delta ht/\text{specific volume} = \text{ft} \times \text{lb/ft}^3 = \text{lb/ft}^2$$

The specific volume of a gas is a function of the pressure and temperature of the gas. The Equation of State for an ideal or perfect gas ($PV = RT$), which will be developed later, indicates the following relation:

$$V = RT/P \tag{1}$$

where V is the volume per unit quantity of medium, ft^3/lb or $ft^3/mole$,
P is the absolute pressure, lb/ft^2,
T is the absolute temperature, degrees Rankine (°R), and
R is the gas constant which depends on the unit quantity of material involved; 53.4 ft-lb/(°R × lb) for air or 1545 ft-lb/(°R × mole)* for any ideal gas.

Then, the decrease in pressure for the increase in height† is

$$-\Delta P = \Delta ht/V = \Delta ht \times P/RT \tag{2}$$

and decreasing the increment of pressure and height to the limit,

$$d(ht) = -RT(dP/P) \tag{3}$$

Assuming the temperature to remain constant and integrating,

$$ht_2 - ht_1 = RT \ln (P_1/P_2) \tag{4}$$

Example.—A column of gas 2,000 ft high exerts a pressure of 10,000 lb/ft² at the top of the column. The temperature of the gas is 500° R. The value of the gas constant R is 50 ft-lb/(°R × lb). Determine the pressure at the bottom and 1,000 ft above the bottom of the column.

$$\begin{aligned} ht_2 - ht_1 &= RT \ln (P_1/P_2) \qquad \text{Eq. (4)} \\ 2{,}000 - 0 &= 50 \times 500 \ln (P_1/P_2) \\ \ln(P_1/P_2) &= 0.08 \\ P_1/P_2 &= 1.083 \\ P_1 &= 10{,}000 \times 1.083 = 10{,}830 \text{ lb/ft}^2 \end{aligned}$$

At 1,000 ft above the bottom the pressure will be 10,408 lb/ft². The increment of 408 lb/ft² pressure from the top to the 1,000-ft position is less than the increment of 422 lb/ft² from the 1,000-ft position to the bottom. The weight of the column of gas of unit cross-sectional area is 830 lb, since this is the difference between the forces exerted by the gas at the top and bottom of the column.

Barometric Pressure.—The atmosphere surrounding the earth exerts a pressure on its surface equivalent to the weight of air above a unit area on the earth's surface. The pressure at sea level is normally about

$$14.7 \text{ lb/in.}^2, \text{ or } 2{,}116.8 \text{ lb/ft}^2$$

being less at altitudes above sea level (Table III Appendix) and more at elevations below sea level. Also, weather conditions cause changes in the barometric pressure.

At any altitude the barometric pressure is equivalent to the weight of the column of air above the given position. This may be measured by determining the height of the mercury column that can be supported by the atmosphere. The customary procedure is to fill a glass tube, closed at one end, with mercury, and then invert the tube so that the open end is immersed in a mercury bath (Fig. 3). The mercury flows from the tube into the bath until the column of mercury is sufficiently high to balance the air pressure, a slight error being introduced by the pressure of the mercury vapor that forms in the tube above the column. It is obvious that the mercury column is being balanced by the pressure exerted by the atmosphere. Therefore,

---

* This is read "foot-pounds per degree Rankine per mole."

† It is seldom necessary to consider the variation in pressure with the height of a gas column in ordinary thermodynamic calculations. However, in the analysis of processes at various altitudes on the earth's surface or in aircraft, this effect on atmospheric pressure must be considered. See Barometric Pressure.

$$\text{Atmospheric pr} = \text{Hg ht} \times \text{Hg sp wt} + \text{negligible Hg vapor pr} \qquad (5)$$

or

$$\text{Atm pr, lb/in.}^2 = \text{Hg ht, in.} \times 0.491 \text{ lb/in.}^3,$$

0.491 being the weight of 1 in.^{3} of mercury.

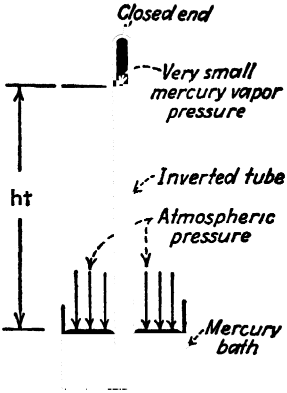

FIG. 3.—Mercury barometer.

The atmospheric temperature (Table III) decreases with altitude from an assumed standard of 59 F at sea level to about −67 F at about 35,000 ft altitude. This indicates a decrease of about 3.6 F per 1,000 ft increase in altitude. Substituting for T, in Eq. (3), its equal in terms of height and sea-level temperature, and then integrating, results in an expression that can be used to estimate the barometric pressure at altitudes up to 35,000 ft.

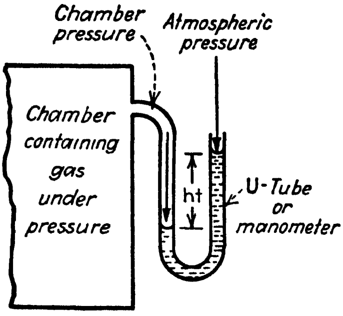

FIG. 4.—U tube or manometer.

Measurement of Pressure.—Pressures slightly below or above atmospheric are usually measured with U tubes which are a form of manometer (Fig. 4). One end of the U tube is connected to a chamber containing the fluid exerting the pressure, while the other end is open to the atmosphere. A liquid in the U tube is displaced because of pressure difference, and the difference in elevation of the menisci of the liquid columns is a measure of the difference in pressure between the fluid in the chamber and the atmosphere surrounding it. Thus,

$$\text{Chamber pr} = \text{man pr} + \text{atm pr} \qquad (6)$$

Bourdon-tube pressure gages (Fig. 5) are used for measuring relatively low to very high pressures. The Bourdon tube, which is curved, fixed at one end, and closed at the other, is surrounded with air at atmospheric pressure. The fixed end of the tube is connected to the chamber in which the pressure is to be determined. The position of the free end of the tube is determined by the difference between the pressures inside and outside the tube. The indicating mechanism attached to the free end of the tube is set to read zero pressure with atmospheric pressure both inside and outside the tube.

Very accurate measurements of pressure are made with piston pressure gages which are also used to calibrate Bourdon-tube pressure gages. The piston fits very closely the cylinder into which the pressure to be measured is transmitted. The piston is loaded with accurate weights until the weight of the piston and the weights balances the pressure exerted on the piston. The piston is rotated during measurements to eliminate friction effects. Thus, all pressures except atmospheric are measured usually as pressures above or below atmospheric and are called *gage pressures*. However, gage pressure is not a pressure but merely the difference between two pressures.

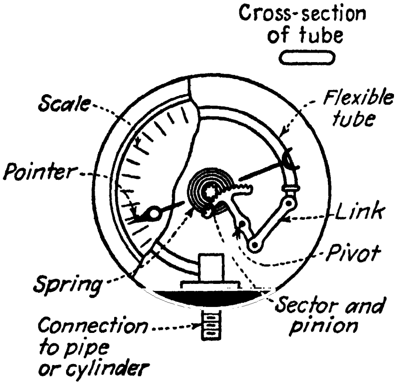

FIG. 5.—Bourdon-tube pressure gage.

Absolute Pressure.—A manometer, attached to a chamber in which gaseous pressure exists, indicates that the algebraic sum of the atmospheric pressure and that equivalent to the manometer column is required to equal the gaseous pressure. Consequently, the total or absolute pressure in the chamber is the sum of the measured pressure and the barometric pressure. Thus,

$$\text{Abs pr} = \text{gage pr} + \text{barometric pr} \tag{7}$$

The absolute pressure is the pressure of the gas on the surrounding surfaces. Consequently, *the absolute pressure must always be used* in thermodynamic analysis.

Example.—The pressure gage attached to a steam boiler indicates a pressure of 375 lb/in.^{2} The barometric pressure is indicated by a column of mercury 30.4 in. high. Determine the pressure of the steam in the boiler.

$$\begin{aligned} 1 \text{ in. Hg} &= 0.491 \text{ lb/in.}^2 \\ 30.4 \text{ in. Hg} &= 14.9 \text{ lb/in.}^2 \\ \text{Abs pr} &= 375 + 14.9 = 389.9 \text{ lb/in.}^2 \end{aligned}$$

Example.—The mercury manometer attached to a steam condenser indicates a vacuum of 29.2 in. Hg. Determine the pressure of the steam in the condenser when the barometer indicates an atmospheric pressure equivalent to 30.4 in. Hg.

Since the mercury column indicates a pressure in the condenser less than atmospheric

$$\text{Condenser pr} + \text{manometer pr} = \text{atm pr}$$
$$\text{Condenser pr} = (30.4 - 29.2)\text{ in. Hg} = 1.2\text{ in. Hg}$$
$$1.2\text{ in. Hg} \times 0.491\text{ lb/in.}^2\text{ per in. of Hg} = 0.59\text{ lb/in.}^2\text{ abs pr in the condenser.}$$

Temperature.—Temperature is a measure of the molecular activity of a medium. The actual molecular activity is not measured, but its effect is evaluated by the change in some property of the temperature-measuring medium, or instrument, with a change in molecular activity.

A mercury thermometer upon immersion in a hot fluid is in contact with the fluid molecules. The motion of the molecules in the hot fluid increases the molecular activity of the glass and mercury of the thermometer until a state of thermal equilibrium is attained in the ideal case. The result of this increase in molecular activity is to expand the mercury very appreciably, and also the glass to a much less extent. This net expansion, indicated by a change in position of the meniscus of the mercury column, provides a means for measuring the temperature of the medium relative to certain arbitrarily chosen values.

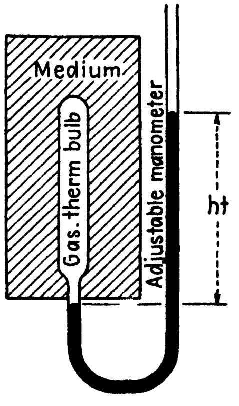

FIG 6.—Elementary gas thermometer.

The medium in a gas thermometer (Fig. 6) may be maintained at constant volume and then will exert a pressure dependent on its state of molecular activity. The bulb of the thermometer is immersed in the medium the temperature of which is desired. A manometer attached to the thermometer bulb can be adjusted so that the volume of the gas remains the same regardless of the pressure. The change in pressure from a known condition provides another means for measuring the temperature of a substance, again relative to certain arbitrarily chosen values.

Various other methods* involving electrical resistance changes, or thermoelectric forces, are used to measure temperature, all of which depend on the change of some property of a medium with a change of molecular activity.

In all cases the medium transfers heat to the thermometer, or vice versa, until thermal equilibrium exists in the ideal case. Thus, mediums in thermal equilibrium with each other are said to be at the same temperature. Also, heat transfer will occur from the medium of higher temperature to a medium at lower temperature.

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* See ZEMANSKY, M. W., "Heat and Thermodynamics," McGraw-Hill Book Company, Inc., New York, 1943.

Thermometer Scales.—Thermometer scales are based on values arbitrarily assigned to the freezing and boiling points of water at a pressure of one standard atmosphere. The Fahrenheit (F) scale has 32 and 212 F, respectively, while the centigrade (C) scale has 0 and 100 C, respectively, assigned to these points (Fig. 7). Obviously, 180 F is the equivalent of 100 C but, in changing from the Fahrenheit to the centigrade temperature scale, 32 deg must be subtracted from the Fahrenheit reading to determine the number of degrees above or below the freezing point before converting the temperature to the centigrade scale. Thus,

$$C = (100/180)(F-32) = (5/9)(F-32) \qquad (8)$$

In converting from centigrade degrees to Fahrenheit, 32 deg must be added after the conversion is made. Thus,

$$F = 9C/5 + 32 \qquad (9)$$

Temperatures lower than the freezing point on the centigrade scale and below zero on the Fahrenheit scale are given negative values (Fig. 7).

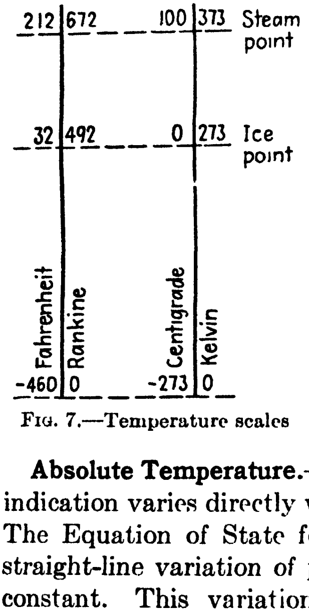

FIG. 7.—Temperature scales

Absolute Temperature.—The constant-volume gas thermometer pressure indication varies directly with the temperature if the gas pressures are low. The Equation of State for an ideal or perfect gas, Eq. (1), indicates a straight-line variation of pressure with temperature if the volume is held constant. This variation of pressure with temperature indicates the possibility of an absolute zero temperature at zero pressure. Thus, extrapolation of the temperature-pressure variation of the gas thermometer between the ice point and the steam point may be used to evaluate the absolute zero temperature in degrees Fahrenheit or centigrade below the ice point.

The perfect-gas thermometer pressure at the steam point is about 1.3661[*] times that at the ice point. Extrapolation of these two values (Fig. 8) indicates an absolute-zero temperature at about 491.7 F below the ice point. Thus, the absolute temperature on the Fahrenheit scale, usually expressed as degrees Rankine (°R) is determined by adding 459.7 F (usually 460 F) to the Fahrenheit temperature (Fig. 7).

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[*] Actual gases approach the perfect-gas state as the pressure approaches zero. Various determinations of this relationship with various gases at lower and lower pressures may be extrapolated to zero pressure to determine the value obtainable if a perfect gas were used.

International Temperature Scale.—An international temperature scale, adopted in 1927 by 31 nations, is based on the use of prescribed thermometers and measurements with these thermometers at the normal melting and boiling points of various substances. The international temperature scale agrees with the perfect-gas thermometer scale at these points, and intervening temperatures are determined from prescribed formulas and indications of the thermometer used.

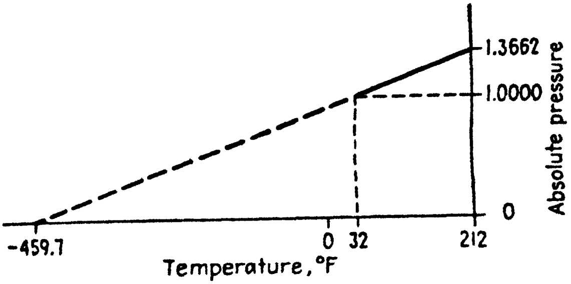

FIG. 8.—Extrapolation of gas thermometer pressure indications.

EXERCISES

1. A cylindrical tank having a base 10 ft in diameter, contains 40 tons of lubricating oil having a specific gravity of 0.9 compared to water at 100 F. Determine the pressure of the oil at the bottom of the tank, the specific volume, and the specific weight of the lubricant. *Ans.* 7.1 lb/in.^{2}; 0.0179 ft^3/lb.

2. A cylindrical tank with its axis in a horizontal position is full of water at 60 F. The tank is 20 ft in diameter and 30 ft long. Determine the total weight of water, the pressure at the bottom of the tank, and plot the volume-height and pressure-depth relationships. *Ans.* 589,000 lb; 1248 lb/ft^2.

3. The tank in Exercise 2 is filled with water. Determine the total force of the water on one end of the tank. SUGGESTION: Plot pressure and end area vs. height of tank. From this graph determine and plot the pressure vs. the end-area relationship. Since force equals pressure times area, the $\int P\,dA$ is the total force on the end of the tank. Evaluate graphically the area beneath the curve on the P vs. A axis to determine the force. *Ans.* 196,000 lb.

4. A tank has an end section described by the following data:

Height, ft.	0	1	2	3	4	5	6	7	8	9	10
Width, ft.	3	5	6.5	6.5	5	4	4	5	7	8.5	9.0

Determine graphically the total force on the end section if the tank is filled with water.

5. A tank has an end section of an inverted isosceles triangle. The base and altitude are both 6 ft. Determine the total force against the end section if the tank is filled with water. Solve analytically and graphically.

6. The atmospheric temperature decreases about 3.6 F per 1,000 ft altitude above sea level. Assuming a straight-line relationship between temperature and altitude, determine the atmospheric pressure at various altitudes up to 40,000 ft, both with and without temperature correction for altitude. Atmospheric pressure and temperature at sea level are 14.7 lb/in.^{2} and 59 F, respectively. Plot pressure and temperature vs. altitude.

7. Determine the pressure of the atmosphere in a mine shaft 10,000 and 20,000 ft below sea level, if sea-level pressure is 14.7 lb/in.^{2} and the temperature is 59 F. Assume constant temperature. *Ans.* 21.3 lb/in.^{2}; 31 lb/in.^{2}

8. Plot the pressure-elevation data obtained from Exercises 6 and 7.

9. A gas column 500 ft high contains air under an absolute pressure of 10,000 lb/in.^{2} at the bottom of the column. Determine the per cent of difference between the pressures at the top and bottom of the column, assuming the perfect-gas relationship. The temperature of the air is 40 F. *Ans.* 1.9 per cent.

10. A tank contains a liquid having a specific gravity of 1.20 compared to water at 60 F. The depth of the liquid is 100 in., there being a 10-in. air space above the liquid. Two gage glasses, *A* and *B*, are connected at one end into the liquid space, the other end of *A* being connected into the air space above the liquid while the other end of *B* is open to the atmosphere. The liquid in *B* stands 100 in. above the top of the tank. Determine the pressure in the air space Barometric pressure is 14.7 lb/in.^{2} *Ans.* 19.46 lb/in.^{2}

11. The column *B* in Exercise 10 has 50 in. of water in it. Draw a sketch showing the location of the water provided it does not mix with the liquid in the column; also locate the top of the column in *B* if the same pressure exists in the air space in the tank as in Exercise 10. What assumptions are made in solving this problem?

12. A conical column 21 ft high and having a base 1 ft in diameter contains 10 ft of mercury, 10 ft of water, and 1 ft of air. Two pressure gages are located at the base of the column, one connecting directly into the column at this level, the other being connected to the air space. Another pressure gage at the top of the column, connected into the air space, indicates 100 lb/in.^{2} What do the two gages located at the bottom of the column indicate?

13. Compute the height of a mercury barometer when the atmospheric pressure is 13.5 lb/in.^{2} *Ans.* 27.5 in.

14. What will be the height of a water barometer for Exercise 13? Also for an atmospheric pressure of 14.7 lb/in.^{2}? *Ans.* 374 in.; 407 in.

15. At 100 F water-vapor pressure of about 0.95 lb/in.^{2} will exist above the water column of the barometer in Exercise 14. What effect will this temperature have upon the height of the water barometer in Exercise 14? *Ans.* 381 in.

16. The pressure in a steam boiler is 250 lb/in.^{2} gage. The barometer is 29.9 in. Hg. Determine the absolute pressure in the boiler. *Ans.* 264.7 lb/in.^{2}

17. The manometer attached to a steam condenser indicates a vacuum of 1.2 in Hg. The barometer is 29.9 in. Hg. Determine the absolute pressure in the condenser. *Ans.* 14.1 lb/in.^{2}

18. Two pipe lines are parallel with each other but line *B* is located a few feet to the right and 10 ft above line *A*. A U tube is located above the two lines and the mercury in it has a difference in level of 20 in. The high side of the mercury manometer is connected into the top of line *B*, while the low side is connected into the top of line *A*. The low side of the mercury in the manometer is 20 ft above the center of line *A*.

a. Determine the difference in the pressures in lines *A* and *B*, assuming the pipe lines and the connecting lines to the manometer are filled with H_2O.

b. Same as (*a*) except that the H_2O in the connecting lines extends 20 ft above the center line of line *A*, and air occupies the remainder of the connecting lines.

19. Compute the value of absolute zero on the Fahrenheit scale from the hydrogen-thermometer data given in the text.

20. Change the following temperatures to equivalent values on the three other scales: −60 F, 500°R, −10 C, and 200 K.

CHAPTER II

ENERGY AND ENERGY TERMS

Thermodynamics deals with the various forms of energy and the transformation from one form to another. Consequently, in the study of this subject, it is essential that the various forms of energy be understood and that the terms applied to them be adhered to very rigorously.

Energy.—A medium, in the solid, liquid, or gaseous state, is said to possess energy when because of its position, motion, or condition it is capable of doing work or of producing an energy effect on other mediums. Thus, the energy of a medium, or a system of mediums, may be defined by the work or other energy effects that can be obtained from the various forms of energy possessed by the medium.

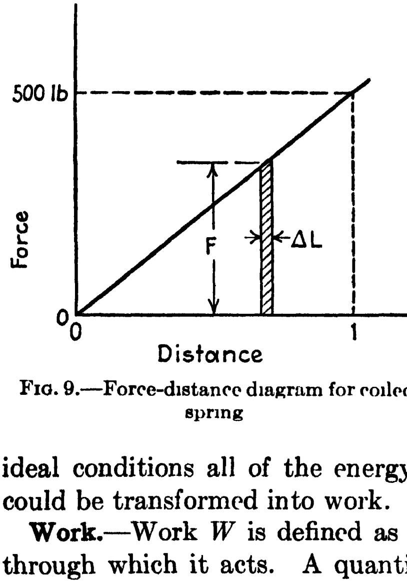

FIG. 9.—Force-distance diagram for coiled spring

This does not mean that under actual conditions all of the energy possessed by a medium can be transformed into work, but that under certain assumed ideal conditions all of the energy, theoretically as a limiting condition, could be transformed into work.

Work.—Work W is defined as the product of a force and the distance through which it acts. A quantity of medium is attracted to the earth by the force of gravity. To lift the medium 1 ft above the earth's surface will require a force at least equal to that of the gravitational attraction, and this force must act through a distance of 1 ft. More work will be required if the material is raised to a higher elevation, being directly proportional to the distance through which the force acts. Hence,

$$\text{Work} = \text{force} \times \text{distance} \tag{1}$$

The units of force and distance are the pound and foot, respectively, which makes the foot-pound (ft-lb) the unit of work. Since work is a form of energy, one of the dimensions that may be used for energy is the foot-pound.

In the foregoing illustration of work, the force may be assumed to be constant for most elevations considered. However, the force may vary with the distance as in the case of compression or expansion of a coiled spring. If the spring is designed to have the force vary directly with the deflection, the force is zero at the beginning of compression and is the product of the scale of the spring, in pounds per foot of deflection, and the deflection at the end of compression. The work done is equal to the mean force times the distance through which the variable force acts.

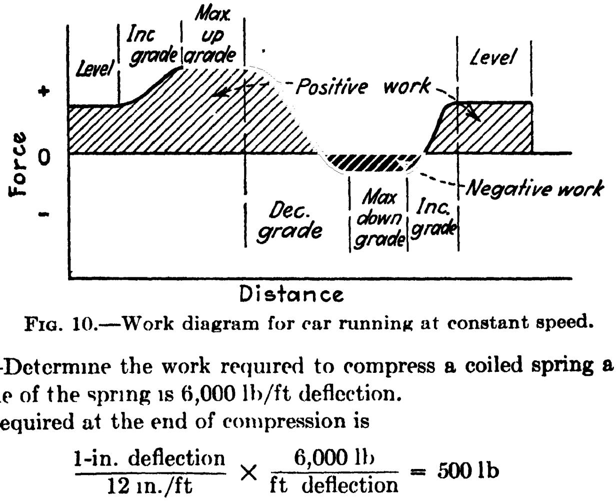

FIG. 10.—Work diagram for car running at constant speed.

Example.—Determine the work required to compress a coiled spring a distance of 1 in., if the scale of the spring is 6,000 lb/ft deflection.

The force required at the end of compression is

$$\frac{\text{1-in. deflection}}{12\text{ in./ft}} \times \frac{6{,}000\text{ lb}}{\text{ft deflection}} = 500\text{ lb}$$

$$\text{Work} = \frac{0 + 500}{2}\text{ lb} \times \frac{1\text{ in.}}{12\text{ in./ft}} = 20.8\text{ ft-lb}$$

The force required for the compression of the spring in the foregoing example is plotted (Fig. 9) on rectangular coordinates, using force as the ordinate and distance as the abscissa. For any small increment of distance ΔL, the mean force is F, and the increment of work is $F\,\Delta L$. This is also the increment of area beneath the path.

The summation of all the small increments of area beneath the curve and the two limiting ordinates results in the total area which is equivalent to the total work of compressing the spring.* The mean force is that force which if acting through the same distance would result in the same amount of work. This is obtained by dividing the work area by its length. This is obviously the average of the forces at the beginning and end of the process in the foregoing example.

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* It should be noted in this and other cases, where the amount of energy is defined as the product of one term times the change of another, that the area representing the quantity of energy is between the path describing the process and the axis used to indicate the coordinate or factor that undergoes the change. Although both terms may vary during a process, as illustrated in Fig. 9, the area between the path and the F axis does not represent the work since work is not defined as distance times the change in force.

The force may vary in many ways with the distance through which it acts. The force required to propel an automobile varies with its speed as well as with the grade of the road. In traveling over a hilly course at constant speed the force will vary from a maximum up the steepest grade to a minimum down the steepest grade encountered. The work required to propel the car a given distance may be determined by plotting the force required against the distance traveled and evaluating the positive work areas (Fig. 10). The negative work area represents work done by the car on the brakes or in overcoming the various other friction effects, while maintaining a constant speed.

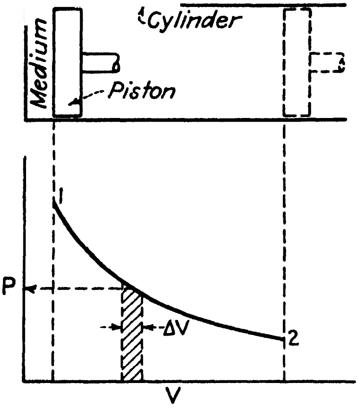

FIG. 11.—Evaluation of work of medium on a piston.

A force always acts along a straight line, and its direction may vary appreciably, but the work will always be the product of the force times the distance through which it acts.

Example.—The force F at radius r at the shaft of a machine acts through a distance $2\pi r$ per revolution. The work per revolution is $2\pi rF$. If the force is variable, it can be plotted as the ordinate against $2\pi r$ as the abscissa, and the work evaluated as the area beneath the path.

A medium, in the liquid, vapor, or gaseous state, may be used to exert a pressure against a piston in a cylinder. If the unit pressure is P and the piston area is A units, the total force on the piston is $P \times A$. Now, if the piston moves through a distance L, the work done is $P \times A \times L$. However, the product of piston area and length of stroke equals the volume displaced or *change in volume*. Thus,

$$\begin{aligned}\text{Work} &= P \cdot \Delta V \qquad (2)\\ &= \text{pressure} \times \text{volume change}\end{aligned}$$

Again, since work is the product of two factors, it may be determined by plotting the force exerted on the piston per unit area (pressure) as the ordinate, against volume as the abscissa (Fig. 11) and evaluating the area beneath the curve and the two limiting volume ordinates, either by graphical or mathematical integration. Thus

$$\text{Rate of flow} = wA/V, \text{lb/sec}$$

Plotting the various instantaneous rates of flow against time and integrating the area between the curve and the time axis (Fig. 13) result in the total weight of fluid passing the section in the given time interval.

The instantaneous values of PV may be plotted against the weight of fluid that has flowed past the given section since the beginning of the process, and the flow work may be evaluated by the area (Fig. 14) between the path describing the variation of PV and the axis indicating the amount of fluid. Thus,

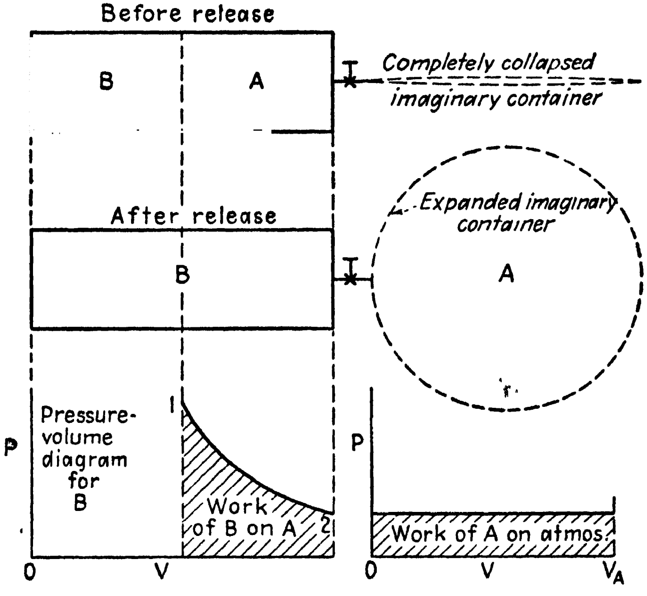
Before release
B
A
Completely collapsed imaginary container
After release
B
Expanded imaginary container
A
P
Pressure-volume diagram for B
1
2
Work of B on A
0
V
P
Work of A on atmos.
0
V
V_A

FIG. 15.—Evaluation of special case of nonsteady-flow work.

$$\text{Nonsteady-flow work} = \int_{\text{wt}_1}^{\text{wt}_2} PV\, d\text{wt} \tag{6}$$

One common case of nonsteady flow is that of no flow at the beginning and end of the process but with flow in between. The release of a medium at high pressure from a chamber to the atmosphere and the reverse flow of the atmosphere into an evacuated chamber are illustrations of this type of process. In the former case, the medium may be divided into two parts: A (Fig. 15), the part that will escape from the chamber when the valve is opened, and B, the part that will remain in the chamber.

When the valve is opened, part B exerting its pressure against part A

pushes it out of the chamber and the pressure in the chamber decreases to atmospheric. Part B does work on part A as shown by the area beneath the path indicating the change in pressure and volume of part B. The dividing line between the two parts is assumed to be an imaginary piston against which part B acts and which in turn acts on part A.

Part A, after escaping from the chamber, occupies a definite volume V_A at atmospheric pressure. In occupying this volume, part A has pushed back the atmosphere and consequently has done work on the atmosphere amounting to $P_{\text{atm}}V_A$. In this analysis it is usually assumed that part A is contained in an imaginary envelope so that mixture with the atmosphere cannot occur.

Potential Energy.—The potential energy, PE, of a body or quantity of medium is determined by its position above the earth's surface, or above any datum plane. Thus, the term *potential energy* of a medium is used exclusively for gravitational energy. This is at variance with the use of the term in mechanics (potential energy of a compressed spring) and in physics (intermolecular potential energy, Fig. 149). The potential energy of a medium is equal to the work that can be done by lowering the medium from the given position to the earth's or other datum surface. The force is that due to the attraction between the earth and the medium and is equal to the weight of the medium. The elevation of the body above the datum surface is the distance through which the force may act. The maximum possible work is the product of these two factors and is termed the *potential energy* of the medium. For a unit weight of 1 lb, the potential energy in foot-pounds is equal to the elevation of the body in feet.

Kinetic Energy.—Kinetic energy, KE, is the energy of a body associated with its motion. This is measured relative to the motion of the earth. It is equal to the work that can be done in bringing the body to rest. This, again, is equal to the product of the force required to stop the body and the distance through which it acts.

The force of gravity can produce an acceleration of g ft/sec^2 on a body of any weight if not influenced by any other forces such as air resistance. Thus,

$$\text{Force of gravity} = \text{mass} \times \text{accel} = \frac{\text{wt}}{g} \times g = \text{wt of body}$$

Another force would produce a proportionately different acceleration of the same body. Thus,

$$\text{Force} = \frac{\text{wt}}{g} \times \text{accel}$$

Hence the work done in decelerating a body from an initial velocity to rest would be

$$\text{Work} = \left(\frac{\text{wt}}{g} \times \text{deceleration}\right) \times \text{distance}$$

$$\text{But, deceleration} = \frac{\text{change of velocity}}{\text{increment of time}} = \frac{dw}{dt}$$

$$\text{and} \qquad \text{Distance} = \text{velocity} \times \text{increment of time} = w\,dt$$

Thus, the increment of work is

$$dW = \left(\frac{\text{wt}}{g} \times \frac{dw}{dt}\right) w\,dt = \frac{\text{wt}}{g} w\,dw$$

$$\text{or} \qquad W = \int_{w_1}^{w_2} \frac{\text{wt}}{g} w\,dw = \text{wt}\left(\frac{w^2}{2g}\right)_{w_1}^{w_2} \text{ft-lb} \qquad (7)$$

If w_2 is zero, the work amounts to $-\text{wt}\cdot(w_1^2/2g)$, the minus sign indicating a decrease in kinetic energy of this amount. Thus, the kinetic energy of a body with a velocity of w ft/sec is

$$KE = \text{wt}\left(\frac{w^2}{2g}\right)\text{ft-lb} \qquad (8)$$

Example.—A train is traveling at the rate of 100 ft/sec. Determine the kinetic energy per ton of train weight.

$$KE = \text{wt}\left(\frac{w^2}{2g}\right) = 2{,}000 \text{ lb} \frac{(100 \text{ ft/sec})^2}{2 \times 32.2 \text{ ft/sec}^2}$$

$$= 310{,}559 \text{ ft-lb}$$

Internal Energy.—The internal energy, U, of a medium is defined as the algebraic summation of the kinetic and potential energy of its molecules. Monatomic molecules have motion of translation and molecular spin, the latter being negligible in amount of energy. Diatomic and more complicated molecules have motion of translation, external and internal rotation, and vibration of the atoms of the molecule.

The molecules in a solid are closely arranged, and any attempt to compress or expand the solid requires a force. Hence the force between the molecules is repulsive when close together and attractive when farther apart (see Fig. 149). Thus, the potential energy of the molecules is negative when close to each other.

A coiled spring, when compressed, has stored in it a definite amount of internal energy as a result of the compression that changed the molecular configuration.

Spectroscopic analysis of vapor or gaseous mediums at various temperatures discloses the macroscopic state of the medium; from this information and the use of statistical mechanics the internal energy of mediums in the vapor or gaseous state may be computed. Internal-energy values obtained in this manner are more accurate than those obtained from the older classical heating experiments and resultant specific-heat equations, particularly at high temperatures. (See the chapter on Properties of Mediums for information regarding the evaluation of internal energy by the heating method.)

Internal-energy values for various mediums under various conditions are given in the Appendix. These values are measured above an arbitrary datum condition, at which the medium is said to possess zero internal energy, although its internal energy is far above zero at this condition. Absolute values of internal energy above the perfectly crystalline state of the substance at absolute zero temperature have been established for some mediums.

Heat.—Internal energy may be transferred from one medium to another because of a temperature difference between the two mediums. This transfer of energy may be accomplished by conduction, convection, or radiation. The total energy transferred in this manner is called *heat*, Q, regardless of the fact that all of the energy transferred may not have been in the form of internal energy in the hot medium at the beginning of the process, or be in this form in the cold medium at the end of the process. A simple illustration of this is the heating of a gas at constant pressure. The gas receives heat which increases the internal energy of the gas, causing it to expand and do work on the surrounding medium or mechanism. Some of the heat transferred remains as internal energy in the medium, but some is transformed into work and leaves the medium.

Work may be dissipated easily by a friction process which results in an increase in internal energy of the mediums involved in the friction process. Joule proposed and conducted experiments to determine the relation between work and heat. These experiments consisted of the expenditure of a known amount of work in stirring water and the evaluation of the resultant equivalent heating effect on the water, its container, and other apparatus affected. Refined experiments of this nature indicate the *mechanical equivalent of heat* to be about 778 ft-lb/Btu.

The dependency of the foregoing relationship upon the property of a medium and the attendant inherent experimental error led to the recommendation, in 1929 at the International Steam Table Conference, of defining the metric heat unit, the calorie, as being 1/860 watt-hr. This defines the Btu as 778.26 ft-lb of energy and eliminates the necessity of further experimental determination of the mechanical equivalent of heat.

Specific Heat.—The transfer of heat to or from a medium manifests itself by either a *change in temperature* or a *change of state of aggregation* (*i.e.*, from solid to liquid, or liquid to vapor state, or vice versa). Thus *change of temperature* is a measure of the addition or abstraction of heat from a medium when not undergoing a change of state of aggregation.

Experience has shown that the amount of heat required for a definite change of temperature of a medium depends upon the quantity or weight[*] of medium involved as well as the nature of the substance. The amount of heat required to change the temperature of a unit weight of medium a unit amount, when a change of state of aggregation does not occur, is called the *specific heat* of the medium. Thus,

$$\text{Specific heat} = \frac{\text{heat transferred}}{(\text{unit wt}) \times (\text{unit temp diff.})} \tag{9}$$

or, in symbols and dimensions,

$$c = \frac{Q\ \text{Btu}}{(M\ \text{lb or moles})\ (T_2 - T_1)\ \text{deg.}} \tag{10}$$

Thus, specific heat, c, is Btu/(lb or mole × °F diff.).

Heat transfer may occur during any process. When it occurs during constant-volume or constant-pressure processes, the symbols c_V and c_P, respectively, are used for the two specific heats.

Example.—The specific heat of air at constant pressure and atmospheric temperature is about 7.0 Btu/(mole × °F diff.). How much heat is required to increase the temperature of 1 lb of air 100 F at constant pressure? One mole of air is 28.97 lb.

From Eq. (10),

$$\begin{aligned} Q &= Mc_P(T_2 - T_1) \\ &= \frac{1\ \text{lb}}{28.97\ \text{lb/mole}} \times \frac{7\ \text{Btu}}{\text{mole} \times {}^\circ\text{F diff.}} \times 100\ \text{F} \\ &= 24.2\ \text{Btu} \end{aligned}$$

Variable Specific Heat.—The addition of heat to a monatomic medium results in an increase in the kinetic energy of translation of its molecules. According to the kinetic theory,[†] the kinetic energy of a monatomic gas is directly proportional to the product of P and V. The Equation of State for a perfect gas indicates that the product of P and V is directly proportional to the absolute temperature. Thus, the specific heat of a perfect monatomic gas is constant. The values of c_V and c_P for such gases are 3.0 and 4.986 Btu/(mole × °F diff.), respectively, for wide ranges of temperature.

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[*] Weight is the force of attraction between the earth and the quantity of medium. Since the force and consequently the weight of a quantity of medium vary with altitude, weight and quantity of medium are synonymous only at a definite datum plane or altitude.

[†] See any standard physics text.

Diatomic gases and others with more than two atoms undergo energy increases because of heating that appear as translational, rotational, and vibrational effects. The latter two effects necessitate more heat addition per degree temperature rise as the temperature is increased. Thus, these gases have variable specific heats that increase with temperature, the difference between c_P and c_V being the constant 1.986 Btu/mole, for perfect gases (see page 54). Specific heats of actual gases vary also with pressure particularly at temperatures near those of liquefaction (see Appendix). At low pressures the specific heat of these gases can be represented as a function of temperature alone. One common form of this relation is

$$c = a + bT + fT^2 \tag{11}$$

Another form is

$$c = a + b/T + f/T^2 \tag{12}$$

where a, b, and f are constants.

For variable specific heat, Eq. (10) may be written*

$$Q = \int_{T_1}^{T_2} Mc\, dT \tag{13}$$

substituting the expression for variable specific heat and integrating result in the heat transfer for the given temperature limits. If T_2 is greater than T_1, the heat transfer is into the medium and the symbol is Q_{in}; if T_2 is less than T_1, the heat transfer is out of the medium and the symbol is Q_{out}. In both cases the heat transfer is considered positive in sign regardless of the result of the mathematical integration.

Mean Specific Heat.—The heat required to change the temperature of a unit quantity of a medium is determined by a product of two terms: specific heat and temperature change. Consequently, heat transfer may be evaluated on a rectangular diagram (Fig. 16) using specific heat as the ordinate and temperature as the abscissa. The $\int c\, dT$ represents not only the area beneath the curve but also the heat transferred to or from the medium for the temperature change indicated by the temperature limits chosen.

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* The formulation of energy tables for various mediums has eliminated much of this use for specific heat data as will be seen later in the text.

Dividing the area by its length results in a mean height which is called the *mean specific heat.* Thus,

$$\text{Mean specific heat} = c_{\text{mean}} = \frac{Q}{T_2 - T_1} \tag{14}$$

Obviously, the product of the mean specific heat and the temperature difference for which it was determined is equal to the heat required to change the temperature of a unit quantity of the given medium *only* through the specified temperature difference.

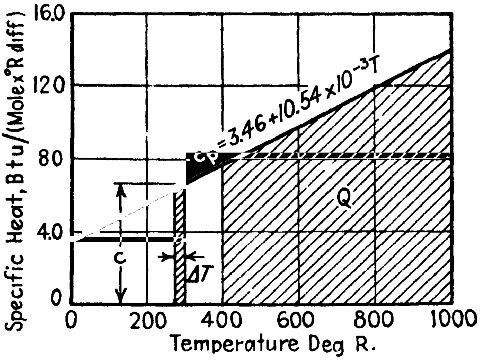

FIG. 16.—Heat diagram. Specific heat vs. temperature.

Latent Heat.—When a pure substance undergoes a change of state of aggregation, the heat required to cause the change is termed the *latent heat.* The change of state may be from solid to liquid, or liquid to vapor, or vice versa, but in any case the process occurs at constant temperature. This eliminates the possibility of using the specific-heat concept for this process.

The term latent heat implies that the heat added to cause the given change remains hidden in the medium undergoing the change. Although most of this energy does remain in the medium undergoing change of state, some energy appears as work done on or by the enclosure surrounding the medium undergoing the change, because of volume increase or decrease, respectively.

Heat Diagrams and Entropy.—It has been shown that the heat transferred to or from a medium can be represented by an area on a specific heat vs. temperature diagram if the temperature of the medium changes with the addition or abstraction of heat. Thus, heat transfer depends on the path representing the process. However, a latent-heat process cannot be represented by an area on this diagram since T does not change and c is infinite according to the definition of specific heat.

An area on a P-V diagram represents work. It is the product of P and ΔV, the former being an intensity factor and the latter indicating a change of a quantitative factor. If heat transfer is to be represented by an area on a diagram, it must be represented similarly by an area that is the product of two factors, an intensity factor and a quantitative factor. Temperature is an intensity factor indicating the possibility of heat transfer in a similar manner to that by which pressure indicates the possibility of work. Then, if heat transfer Q is to be represented by an area, using T as the intensity factor,

$$Q = T \times \Delta\ (\text{second factor}) \tag{15}$$

where T is the ordinate, and the second factor is the abscissa of the diagram on which the area is to be evaluated. Then,

$$\text{Second factor} = \frac{Q\ \text{Btu}}{T^\circ\text{R}} = \Delta S \tag{16}$$

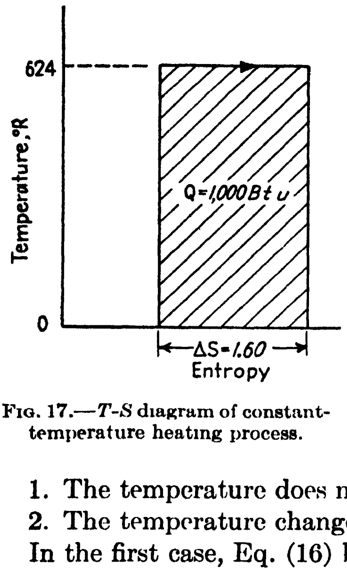

FIG. 17.—T-S diagram of constant-temperature heating process.

The term *entropy change*,* ΔS, has been given to this second factor. Its dimensions as indicated in Eq. (16) are Btu/(lb or mole × °R) whichever quantity of medium is considered. The heat transfer required to change the temperature or state of M lb or moles of material would be M times that required for a unit quantity. Consequently, the entropy change varies directly with the quantity of material.

All heat-transfer processes may be classified as follows:

1. The temperature does not change with heat transfer.
2. The temperature changes with heat transfer.

In the first case, Eq. (16) becomes

$$S_2 - S_1 = Q/T \tag{17}$$

Example.—The latent heat of H_2O at 164 F is 1000 Btu/lb. Determine the increase in entropy in changing 1 lb of H_2O from liquid to vapor at this temperature.

$$S_2 - S_1 = \frac{Q}{T} = \frac{1000\ \text{Btu/lb}}{(164 + 460)^\circ\text{R}} = 1.60\ \text{Btu/(lb} \times {}^\circ\text{R)}$$

A sketch of this process on the T-S diagram results in a rectangular area for Q (Fig. 17).

In the second case, the heat added may be evaluated from the specific-heat relationship. Then,

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* It should be noted that this definition of entropy is elementary yet fundamental to the portrayal of heat-flow processes. The more significant meaning of entropy will be discussed later in the chapter on Availability of Energy.

$$\Delta S = \frac{Q}{T} = \frac{Mc\,\Delta T}{T} \tag{18}$$

and,

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{Mc\,dT}{T} \tag{19}$$

Example.—Determine the increase in entropy and heat added to 1 lb of H_2O in being heated from 40 to 340 F, assuming a constant specific heat of $c = 1$ Btu/(lb × °F).

$$S_2 - S_1 = \int_{500^\circ\text{R}}^{800^\circ\text{R}} 1 \times 1 \times \frac{dT}{T} = \ln\frac{800}{500} = 0.470 \text{ Btu/(lb} \times {}^\circ\text{R)}$$

Also,

$$Q = Mc(T_2 - T_1) = 1 \times 1 \times (800 - 500) = 300 \text{ Btu}$$

A plot of this process on a T-S diagram (Fig. 18) results in a curve that is concave upward. It should be noted that with constant specific heat the change of entropy per degree change of temperature is less the higher the temperature. The area beneath the curve, between the limiting ordinates and down to absolute zero temperature, represents the 300 Btu of heat transferred to the medium during the heating process.

With variable specific heat the expression for c in terms of T must be substituted before integration.

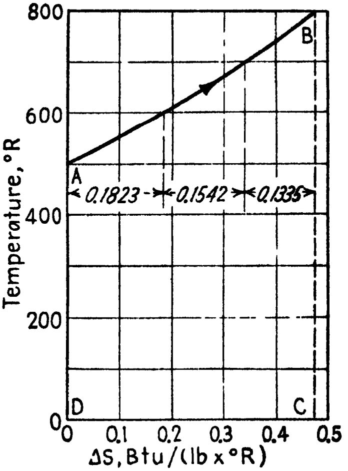

FIG. 18. T-S diagram of heating process. Note values for ΔS for 100 F increments.

Example.—Determine the entropy change for 1 mole of CO_2 in being heated at constant pressure from 40 to 340 F. The specific-heat equation per mole of CO_2, as given by Sweigert and Beardsley (Appendix), is

$$c_P = 16.2 - 6.53 \times 10^3/T + 1.41 \times 10^6/T^2$$

Substituting this expression for c in Eq. (19) and integrating result in

$$S_2 - S_1 = \Big[16.2 \ln T + 6.53 \times 10^3/T - 0.705 \times 10^6/T^2\Big]_{500^\circ\text{R}}^{800^\circ\text{R}}$$

Substituting the limits results in

$$S_2 - S_1 = 7.614 - 4.897 + 1.718 = 4.435 \text{ Btu/(mole} \times {}^\circ\text{R)}$$

The path of the process with variable specific heat is similar to that with constant specific heat, but with less curvature of the path because of more heat being required per degree at the higher temperatures.

Entropy, like internal energy, is usually measured above, or below, an arbitrarily chosen datum plane or condition that is assigned a value of zero entropy. When heat is added, the entropy of the medium increases; when heat is rejected, the entropy decreases if fluid-friction effects are not present.* For a frictionless process the area beneath the path represents the heat transfer into or out of the medium, depending on the direction in which the process is moving on the T-S diagram. Obviously, a frictionless *adiabatic* process, in which there is no heat transfer, is represented by a vertical line on the T-S diagram.

Although the foregoing method of evaluating heat transfer by an area on a T-S diagram is valid for any given frictionless process, it remains to be proved that entropy is a point function that can be used as a coordinate to describe a medium since, in the foregoing, entropy change is evaluated by the quotient of a quantity Q that depends on the path and a coordinate T. Consequently, no assurance is given in this development that entropy is not a function of the path, although later (Chap. VII) it is shown to be a point function and can therefore be used as a coordinate.

Radiant Energy.—Radiant energy is transferred from one medium to another by electromagnetic waves of various frequencies. These waves may be produced in various ways, one of which is by the application of heat. Actually, all solids, liquids, and some gases emit radiant energy at any temperature, and the effect of an increase in temperature is to increase the radiation very appreciably.

A medium that radiates will also absorb radiant energy. The evaluation of the net radiation emitted or absorbed by a medium because of its temperature and that of the surrounding mediums is an involved process.† However, when evaluated, radiant energy is treated the same as heat transferred in or out of the medium considered.

Chemical Energy.—When molecules of some mediums collide with each other under certain conditions, a reaction takes place that results in molecules of other substances. Such a reaction usually results in the liberation or absorption of energy because of the changes in bonding arrangements of the various molecules in combining or breaking up to form other molecules. This energy liberation or absorption is termed *chemical energy*. It is designated by the symbol C with a subscript indicating the reaction considered.

The *heat of reaction* is the heat transfer required to maintain a constant-temperature reaction process or to return the products of the reaction to the original temperature of the constituents before the reaction. The heat of reaction, like heat transfer, depends on the process (constant volume or pressure, etc.) while the chemical energy of the reaction depends only on the original and final bonding arrangement. Thus, chemical energy does not depend on the path but is a point function. Chemical energy will be equal to the heat value when the energy values of the mediums before reaction are equal to the energy values of the products after the process. (See the chapter on The Combustion Process.)

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* It will be shown in the chapter on Availability of Energy that friction processes result in an increase in entropy without heat transfer into the medium.

† See McAdams, W. H., "Heat Transmission," McGraw-Hill Book Company, Inc., New York, 1942.

Electrical Energy.—Electrical energy is analogous to work or heat because it is the product of two factors, one of which is the electromotive force while the other is the quantity of electricity. The units of the two factors are the *volt* and the *ampere-second*, respectively. Then

$$\begin{aligned}\text{Electrical energy} &= \text{volts} \times \text{amp-sec} \\ &= \text{watt-sec}\end{aligned}$$

the watt-second being the unit of electrical energy. It is equivalent to 0.738 ft-lb of energy.

In most thermodynamic processes electrical energy is transformed immediately into heat or into work and heat and may usually be treated as such.

Energy Terms; Functions of State or Process.—The potential energy stored in an automobile on top of a given mountain is the same regardless of the road or path followed in arriving at the mountain top. Likewise, it can be shown that the kinetic, internal, and chemical energy of a medium are determined by either the position, motion, or condition of the medium, irrespective of the manner or path by which the medium arrived at its position, motion, or condition. Thus, these forms of energy are said to be functions of the state of the medium, and consequently, *only the state of the medium need be known to evaluate potential, kinetic, internal, and chemical energy.* Steady-flow work is also a function of the state since it is equivalent to the product of two coordinates, P and V.

Work, heat, and electrical energy are each the product of two factors that are unrelated and vary independently of each other. The variation of these factors is illustrated when the process in question is plotted on a diagram using the two factors as coordinates. Also, it has been shown that the areas beneath such paths, when plotted according to the conventions indicated, are measures of these forms of energy. Thus, these energy terms are said to be functions of the path or of the process that the medium is undergoing. Consequently, not only the initial and final states of the medium but also *the path of the process must be known to evaluate work, heat, and electrical energy.*

Energy Units.—It is apparent from the foregoing that a number of different energy units may enter into a solution of an energy problem. It has been shown that the various energy units are related. Table I (Appendix) summarizes these relationships.

It is fundamental that the dimensions of each term of an equation are the same. The use of symbols representing energy quantities, in setting up thermodynamic relationships, implies that the *dimensions of the symbols make the relationship dimensionally consistent.* The substitution of numerical values for the symbols necessitates the checking for dimensional consistency which can be done by substituting the dimensions with each numerical value.

EXERCISES

1. The torque of an internal-combustion engine is 200 lb-ft at 3,000 rpm. This indicates a force of 200 lb at a radius of 1 ft. Determine the horsepower developed by the engine at 3,000 rpm. *Ans.* 114 hp.

2. The engine in Exercise 1 has 12 cylinders with a bore and stroke of 3.5 and 4 in., respectively. Each cylinder has one working stroke every two revolutions. Determine the mean effective pressure. *Ans.* 65.4 lb/in.^{2}

3. A double-acting 10-in. bore and 12-in. stroke steam engine has a mean pressure of 150 lb/in.^{2} abs acting on the piston during each working stroke. The other side of the piston is exhausting against a mean back pressure of 50 lb/in.^{2} abs. The piston rod is 2.5 in. in diameter. Determine the horsepower of the engine at a speed of 500 rpm. *Ans.* 231 hp.

4. A cylinder having a cross-sectional area of 1 ft^2 has a piston with a coiled spring on the side open to the atmosphere. Air is admitted on the other side of the piston until a pressure of 100 lb/in.^{2} gage is attained. During air admission the piston moves 1 ft and compresses the spring a like amount, which is one-half the original length of the spring. The cylinder is then cooled from 600 to 300°R and the piston returns 6 in., reducing the force on the spring 50 per cent. Determine the work done by and on the piston, spring, and atmosphere. *Ans.* Work of gas on piston, 9,320 ft-lb.

5. A medium has its pressure and volume changed so that the path describing the process is a circle on the P-V diagram. The center of the circle is at a pressure of 100 lb/in.^{2} abs and a volume of 100 in.^{3} The diameter of the circle represents a change in pressure of 100 lb/in.^{2} as well as 100 in.^{3} Evaluate the work for a process that takes the point describing the medium around the circle.
Ans. $W_{\text{in}} = 6{,}070$ in.-lb; $W_{\text{out}} = 13{,}930$ in.-lb.

6. A cylinder has a cross-sectional area of 1 ft^2. The piston is at the outer end of the stroke which is 2 ft. A medium at a pressure of 500 lb/in.^{2} abs is in the cylinder. The cylinder is covered with dry ice, and heat is transferred from the medium and its pressure falls to 100 lb/in.^{2} abs. The piston then moves 1 ft at a rate to maintain constant pressure of 100 lb/in.^{2} abs. Determine the work. Is it done on or by the medium?

7. A cylinder 1 ft in diameter contains 1 ft^3 of gas at 100 lb/in.^{2} abs pressure, P_1. A coiled spring is on the other side of the piston in the cylinder and is compressed to exert a pressure of P_1 times the piston area so that the gas cannot move the piston. The stop at the end of the spring is backed off gradually reducing the compression on the spring so that the piston moves and the pressure falls slowly to 50 lb/in.^{2} so that

$P_1V_1 = P_2V_2 = PV =$ constant. Was work done by or on the gas or spring, or stop, or both, and how much? Assume that the spring length increases 1 ft during the process. *Ans.* 10,000 ft-lb.

8. Fifty pounds of gas per second flow through a given horizontal section of a 12-in. diameter pipe line. The gas pressure at the given section is 100 lb/in.^{2} gage. The barometer indicates an atmospheric pressure of 29.92 in. Hg. Evaluate any form of energy possible from the data given. Gas specific weight at section is 0.1 lb/ft^3.

Ans. 8,250,000 ft-lb/sec; 315,000 ft-lb/sec.

9. A 100-ft^3 chamber contains gas under a pressure of 500 lb/in.^{2} abs. A valve at one end is opened and the pressure is reduced very slowly to 250 lb/in.^{2} Only half of the gas escapes to the atmosphere. Evaluate the work that the half of the gas remaining in the tank does on that which flows out. The slowness of the process indicates that the gas temperature in the tank remains constant, and that $PV =$ constant.

Ans. 2,495,000 ft-lb.

10. Assume the data required and evaluate the work of the part of the gas that escapes from the chamber in Exercise 9. Why are the work values different in Exercises 9 and 10?

11. The flow rate of a medium at a given section in a pipe line increases from 10 to 15 lb/sec in 1 min. The pressure decreases from 100 to 50 lb/in.^{2} abs while the specific volume increases from 1 to 1.5 ft^3/lb. All changes plot as straight lines against time. Determine the flow work of the medium passing the section during the minute when the flow rate is increased.

12. Water is being pumped upward through a 3-in. pipe. At one point the pressure is 62.4 lb/in.^{2} abs. At another point the pressure is 124.8 lb/in.^{2} abs. The specific weight of the water is 62.4 lb/ft^3. Evaluate the flow work per pound of medium at both points, and also the maximum possible *PE* change between the two points.

Ans. Flow work = 144 ft-lb/lb of H_2O.

13. How much difference in elevation will result in a change in potential energy equivalent to 1 Btu/lb of substance considered?

14. Compute and plot the kinetic energy of a 2,500-lb automobile at various speeds from 20 to 100 mph. Assuming a coefficient of friction of unity between the tires and the road, compute and plot the stopping distances for the various speeds of the car.

Ans. 30.2 ft at 30 mph.

15. Plot two curves on a graph indicating entering and leaving velocities (the coordinates of the graph) for a difference of kinetic energy of 1 Btu/lb of fluid flowing into and leaving the apparatus. Range 0 to 1,000 ft/sec.

16. Ten pounds of vapor in a chamber at a pressure of 1,000 lb/in.^{2} abs and a temperature of 1000°R condenses at constant temperature while transferring 10,000 Btu of heat through the walls of the chamber to water which rises in temperature from 40 to 540 F. Each pound of water receives 1 Btu of heat per 1 F rise. Determine the change of entropy of the vapor and of the water, and the net change in entropy.

Ans. Net change = 3.862 Btu/°R.

17. The specific heat equation for gaseous H_2O is given in Table II, Appendix.

a. Determine the instantaneous specific heat at intervals of 500 from 500 to 3000°R.

b. Plot the results of (*a*) on a specific heat-temperature diagram.

c. Determine the mean specific heat from 500 to 3000°R, both graphically and analytically.

d. How does the mean compare with the instantaneous specific heat at 1750°R?

18. Plot the path of the process in Exercise 17 on a temperature-entropy diagram and compare the heat added, determined graphically, from 500 to 3000°R, with the result from the specific-heat relationship.

19. A medium does work on a piston while sufficient heat is added to the medium to maintain a constant temperature. The equation of this process is PV = constant. The medium is then cooled at constant pressure to the original entropy. Finally, the medium is compressed to the initial condition during which process no heat is added. Indicate by areas on diagrams the net heat added or abstracted and the net work done on or by the medium.

20. Ice has a specific heat of about 0.5 Btu/(lb × °F diff.). Heat is abstracted from 10 lb of ice and its temperature is reduced from −60 to −260 F. Determine the heat abstracted and the change in entropy for the 10 lb of ice.

21. A hot substance rejects heat at a constant temperature of 2000°R. All of the heat rejected by the hot substance is absorbed at constant pressure by a colder substance which has an initial temperature of 1000°R and a final temperature of 2000°R. The specific heat of the colder substance is 1 Btu/°F diff. per the quantity used. Determine the change of entropy of each substance and the net change, considering both substances.

22. One pound of steam at 212 F and atm pressure is condensed at the same pressure and temperature. Latent heat of 970 Btu is removed during this process. The liquid water is then cooled from 212 to 32 F, which requires the removal of 180 Btu. The liquid water is then frozen at 32 F, which requires the removal of 144 Btu. Determine the total change in entropy.

23. One pound of water at 200 F is in a container which is lowered into another container having 1 lb of water at 100 F. The heat transferred from the hot to the cold water is 50 Btu. The final temperature of both quantities is 150 F. Will there be a net change in entropy and if so compute it? If not, explain.

24. Gas does work on a piston during an ideal adiabatic process (from 1 to 2); then it is heated (from 2 to 3) at constant volume to the original temperature; finally it has work done on it (from 3 to 4) while heat is abstracted until the final condition is reached. $S_1 = S_4$ for the process, and $T_4 > T_1$. Indicate on diagrams the net work done and the net heat transferred. Indicate whether work is done on or by the medium and whether heat transfer is in or out of medium.

25. A substance has no change in entropy but an increase in volume.

a. Does any work occur? Why?

b. Is any heat transferred? Why?

26. Work is done by a gas on a piston while the gas temperature increases. Sketch diagrams of the process and indicate the work and heat areas.

27. A gas in an engine cylinder has its volume changed from 1 to 2 ft^3 by piston motion, the gas pressure remaining constant at 100 lb/in.^{2} gage.

a. Evaluate any energy terms possible and describe them fully.

b. Sketch the process on the T-S diagram.

28. A closed chamber contains a medium. An electrical resistance wire is located in the medium. An electric current flows through the wire. What forms of energy must be dealt with?

29. An automobile engine inducts air and fuel, which are mixed in the carburetor.

a. What forms of energy must be evaluated ahead of the carburetor, and between the carburetor and the engine?

b. What forms of energy leave the engine?

30. A steam turbine is operating under usual conditions. What forms of energy enter and leave the turbine? Draw a diagrammatic sketch of the apparatus and indicate where the forms of energy are evaluated.

31. Air at a pressure of P_1, a specific volume of V_1, and a temperature of T_1 flows steadily into the well-rounded entrance of a pipe line and then into a compressor. The conditions in the pipe line on the discharge side of the compressor are P_2, V_2, and T_2—T_2 being higher than T_1. At some distance downstream from the compressor the condition of the flowing air is P_3, V_3 and T_3—T_3 being equal to T_1. The relation between P, V, and T per unit quanity of air is $PV = RT$, in which R is a constant. Compare the flow work at the three positions in the pipe line and state the source of the flow work in each case.

32. A gun fires a projectile vertically. What forms of energy must be considered?

a. With the projectile leaving the gun?

b. With the projectile at the top of its flight?

c. With the projectile buried in the ground after descent?

33. The gram-caloric is defined as 1/860 watt-hr. Show that this is equivalent to defining the Btu as 778 ft-lb.

34. Check the foot-pound and Btu values for the horsepower-hour and kilowatt-hour units in Table I, Appendix.

CHAPTER III

THE ENERGY EQUATION AND PROCESSES

Principle of Conservation of Energy.—The various forms of energy that may be associated with thermodynamic processes have been defined in Chap. II. These forms of energy, their symbols, and their definitions are summarized as follows:

1. Potential energy, *PE;* energy of the medium because of its elevation above a given datum plane.
2. Kinetic energy, *KE;* energy of the medium because of its motion.
3. Internal energy, *U;* potential and kinetic energy of the molecules of the medium, including rotational and vibratory energy of the molecules.
4. Chemical energy, *C;* energy liberated or absorbed because of chemical reaction.
5. Work, *W*; work done by a medium on a mechanism or vice versa;
    - $\int P\,dV$, where P is the pressure of the medium acting on the piston or other medium;
    - PV, flow work of a medium at a given section in a flow line when P and V are the conditions at the section.
6. Heat, *Q*; energy transferred from a hot to a cold medium because of temperature difference.
7. Electrical energy, *EE;* energy flowing into or out of the medium or apparatus by means of electrical circuits. This may be treated the same as heat.
8. Radiant energy, *RE;* energy flowing into or out of the medium or apparatus from mediums at higher temperatures or to mediums at lower temperatures. This may be treated also as heat.

The universal experience with any of the forms of energy in any process indicates that the disappearance of a given amount of energy of one form results in and coincides with the appearance of the same amount of energy in some other form or forms. A body falling in a vacuum undergoes a decrease in potential energy but gains an equal amount of kinetic energy. A chemical reaction results in a change in the chemical energy of the mediums involved, and this energy change appears as heat transfer be-between the reaction apparatus and the surroundings and a change in the energy content of the mediums and the apparatus. The electrical energy supplied to an electric-light bulb disappears but reappears as heat transfer to the air surrounding the bulb and light energy radiated therefrom. Such experiences resulted in the belief that energy is indestructible or in the formulation of the *Principle of Conservation of Energy* and the *First Law of Thermodynamics* in the broadest sense.

General Energy Equation.—The Principle of Conservation of Energy indicates that the sum of the energy that a medium possesses before a process and the energy added to it during the process must equal the sum of the energy that the medium possesses at the end of the process and the energy taken away from it during the process. Assuming that all the forms of energy previously listed* are involved in a general steady-flow process, the *General Energy Equation* is

$$C_1 + PE_1 + KE_1 + U_1 + P_1V_1 + W_{in} + Q_{in} = C_2 + PE_2 + KE_2 + U_2 + P_2V_2 + W_{out} + Q_{out} \quad (1)$$

All the terms in this equation as written are positive values of energy. The mechanical work and heat-transfer terms are evaluated in ideal cases by areas that are assumed to be positive in sign regardless of the result of the integration of $P\,dV$ or $T\,dS$, respectively. Thus, with the usual mathematical conventions,

$$W_{in} = -\int P\,dV \qquad \text{and} \qquad W_{out} = \int P\,dV \quad (2)$$

while

$$Q_{in} = \int T\,dS \qquad \text{and} \qquad Q_{out} = -\int T\,dS \quad (3)$$

Analysis of Processes.—All processes may be classified as follows for simplification of thermodynamic analysis:

1. Nonflow processes
2. Flow processes
   a. Steady-flow processes
   b. Nonsteady-flow processes

In the analysis of nonflow processes all energy terms in the General Energy Equation are eliminated except C, U, W, and Q. Obviously, C is eliminated for nonreaction processes, and any of the other terms except U may be eliminated depending on the nature of the process.

An imaginary envelope is assumed to be around the medium for which the Energy Equation is to be written. Diagrammatic sketches of the apparatus containing the medium before and after the process should be drawn. Also, P-V, or T-S, or both diagrams illustrating the process should be drawn and work and heat areas should be indicated.

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* Electrical and radiant energy are treated as heat transfer.

Example.—A medium is confined in a steel tank and is at atmospheric temperature. The steel tank containing the medium is placed in a refrigerator and after some time is at the refrigerator temperature. Write the Energy Equation for the process.

Assuming negligible change in volume of the tank on being cooled, the process is one of constant volume. The tank is the imaginary envelope around the medium and is indicated (Fig. 19) both before and after the process. Heat is removed from the medium during the process. Assuming that chemical reaction does not occur, the Energy Equation for this process is

$$U_1 = U_2 + Q_{\text{out}} \tag{4}$$

The heat transfer out may be evaluated from the area under the path representing the process on the *T-S* diagram, or from the specific-heat relationship

$$Q_{\text{out}} = \int_{T_2}^{T_1} Mc\,dT \tag{5}$$

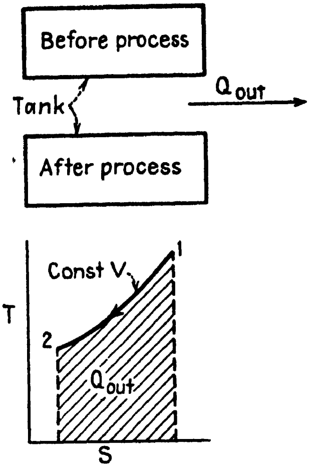

FIG. 19.—Constant-volume cooling.

The medium in a nonflow process may change in volume during the process and do work on, or have work done on it by, a mechanism (Fig. 20).

Example.—High-pressure air at atmospheric temperature in a cylinder acts on a piston and moves it through a given distance. Write the Energy Equation for the process.

Only U, W, and Q terms are involved in this process. The medium does work on the piston and undergoes a decrease in temperature. Thus, any heat flow will be into the medium, and the Energy Equation is

$$U_1 + Q_{\text{in}} = U_2 + W_{\text{out}} \tag{6}$$

The work done by the medium on the piston may be evaluated from the area beneath the path representing the process on the *P-V* diagram if the pressures plotted are those of the medium acting on the piston.

In the *steady-flow process* the medium is flowing at the same steady mass rate into and away from the apparatus in which the process is occurring. An imaginary envelope around the apparatus (Fig. 21) cuts the pipe lines at point 1 where the fluid is flowing into or toward the machine and also at point 2 where the fluid is leaving the machine. The envelope also cuts the lines indicating energy in transition (work, heat, etc.) to or from the medium as it passes through the machine. The condition of the medium flowing at points 1 and 2 remains constant, which indicates that flow work in = P_1V_1 and flow work out = P_2V_2.

If a chemical reaction does not take place in the apparatus, being indicated by the same medium leaving as entering the apparatus, the C

terms are omitted In many cases the potential and kinetic energy changes are small and may be neglected Obviously, this depends on the per cent of error introduced in the result by the omission of these terms Also, the U and PV terms are usually added in such cases, and the sum is termed H, the enthalpy Finally, in many processes only one form of work and heat transfer is involved

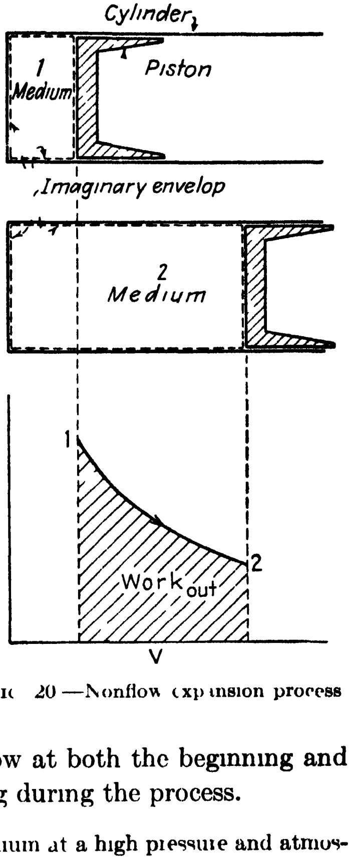

Fig 20 —Nonflow expansion process

Example Air flows steadily through a motor-driven air compressor Write the Energy Equation for the process

The imaginary envelope may surround only the air compressor (Fig 22) No chemical reaction occurs, the PE and KE terms may be assumed negligible The U terms are always present steady flow indicates the PV terms, and work is required to drive the compressor The compression process raises the air temperature, and heat transfer occurs from the compressor to the surroundings Thus

$$U_1 + P_1V_1 + W_{in} = U_2 + P_2V_2 + Q_{out} \quad (7)$$

Since $U + PV = H$ Eq (7) becomes

$$H_1 + W_{in} = H_2 + Q_{out} \quad (8)$$

which is the Energy Equation for the air compressor process

If the imaginary envelope surrounds the electric motor also, the EI_{in} to the motor would be substituted for the W_{in} term The Q_{out} term then would represent the heat losses from the air compressor and the electric motor

The usual *nonsteady-flow process* has no flow at both the beginning and the end of the process, but has flow occurring during the process.

Example.—A tank initially contains a gaseous medium at a high pressure and atmospheric temperature A part of the gas is permitted to escape slowly from the tank to the surrounding atmosphere Write the Energy Equation for the process

The envelope is placed around the part for which the Energy Equation is desired In Fig 23 it is placed around the gas that escapes (part A) both before and after escaping The internal energy of gas A is U_1 before escaping and U_2 after escaping During the escaping process, gas B, which remains in the cylinder, expands and does work on gas A Also, gas A pushes back the atmosphere and does work on it at constant pressure

The heat-transfer effects are not very obvious However, the last part of A to escape undergoes considerable expansion and does work on the earlier parts that escape This reduces its temperature Consequently, heat transfer would occur from the surrounding atmosphere to the tank and into the part of gas A in the tank while the other parts of it are escaping. If part A after escaping is at a mean temperature above atmospheric, heat would flow out of A to the surrounding atmosphere. Since the gas is not flowing at the beginning or at the end of the process, the KE terms are omitted. Thus, the Energy Equation for part A is

$$U_{1_A} + W_{B \text{ on } A} + Q_{\text{in}_A} = U_{2_A} + W_{A \text{ on atm}} + Q_{\text{out}_A} \tag{9}$$

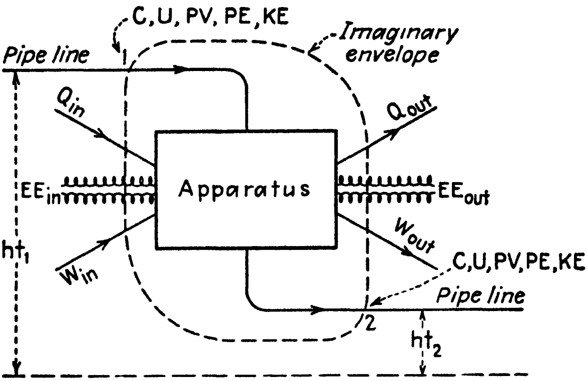

FIG. 21.—Sketch for steady-flow process.

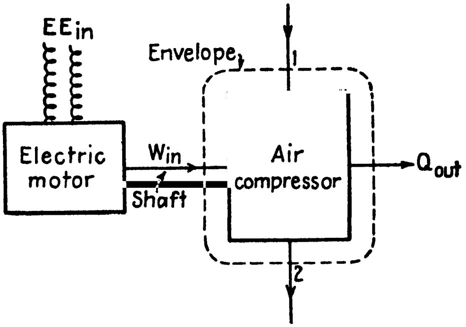

FIG. 22.—Motor-driven compressor.

The work of part B on A may be evaluated from the P-V diagram (Fig. 15) representing the pressure-volume change for part B, while the work of part A on the atmosphere may be evaluated from the other P-V diagram representing the pressure-volume change of the atmosphere. It should be noted that the atmosphere has been displaced by an amount equal to the final volume of part A.

Thus, the Energy Equation for part B is

$$U_{1_B} + Q_{\text{in}_B} = U_{2_B} + W_{B \text{ on } A} \tag{10}$$

Also the Energy Equation for the entire quantity of medium involved is

$$U_1 + Q_{\text{in}} = U_{2A} + U_{2B} + W_{A \text{ on atm}} + Q_{\text{out}} \tag{11}$$

It should be noted that the Energy Equation is written for a definite amount of medium; consequently all terms and dimensions refer to that quantity of medium. Also, the sum of the Energy Equations for the various parts of a medium results in the Energy Equation for the total quantity of medium. Thus, adding Eqs. (9) and (10) results in

$$U_{1_A} + U_{1_B} + Q_{\text{in}_A} + Q_{\text{in}_B} = U_{2_A} + U_{2_B} + W_{A\text{ on atm}} + Q_{\text{out}_A} \qquad (12)$$

which is identical with Eq. (11) since $U_1 = U_{1_A} + U_{2_A}$; $Q_{\text{in}} = Q_{\text{in}_A} + Q_{\text{in}_B}$; and $Q_{\text{out}} = Q_{\text{out}_A}$.

The nonsteady-flow process may be one of variable rates of flow into and out of the apparatus. In such cases it may be necessary to evaluate the various energy terms dependent on flow in a manner indicated in Figs. 13 and 14.

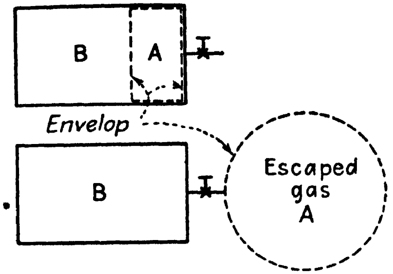

FIG. 23.—Nonsteady-flow process.

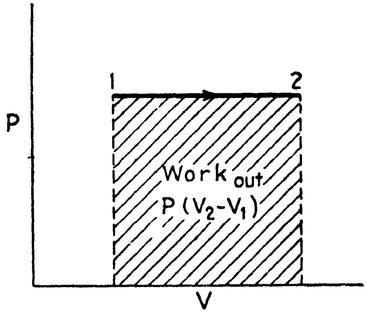

FIG. 24.—Constant-pressure process.

Enthalpy.—In the steady-flow analysis in which the flow work is equal to PV, attention has been called to the practice of combining corresponding U and PV terms, for the same conditions of medium, and representing the sum by H, the enthalpy. Thus,

$$H = U + PV \qquad (13)$$

and enthalpy is a function of the state or condition of the medium, since it is the sum of an energy term that is a function of the state of the medium and the product of two of the coordinates that indicate the state.

The term H appears in the Energy Equation *only for steady-flow processes with two exceptions, the nonflow and the nonsteady-flow constant-pressure processes* in which cases it is introduced by manipulation. The Energy Equation for the nonflow constant-pressure process (Fig. 24) is

$$U_1 + Q_{\text{in}} = U_2 + W_{\text{out}} \qquad (14)$$

for increasing volume, or

$$U_1 + W_{\text{in}} = U_2 + Q_{\text{out}} \qquad (15)$$

for decreasing volume. In the former case

$$W_{\text{out}} = P(V_2 - V_1) = PV_2 - PV_1 \tag{16}$$

Since the pressure is constant, the PV_1 term may be added to U_1, and the PV_2 term to U_2, and Eq. (14) becomes

$$H_1 + Q_{\text{in}} = H_2 \tag{17}$$

It should be noted that a value for H may be computed for any condition for a given medium and is listed in Tables of properties of various mediums for various conditions. However, H appears in the Energy Equations only for the cases indicated.

General Method of Process Analysis.—The analysis of a thermodynamic process usually consists of determining the Energy Equation for the process, evaluating the known energy terms, and solving the Energy Equation for the unknown term. The Energy Equation for the process can be determined and solved only if the process is understood. Consequently, the following steps should be followed:

1. Draw a simple diagrammatic sketch which indicates the general nature of the process.
2. Draw an imaginary envelope around the apparatus through which steady flow of a medium or mediums is occurring. If the process is other than one of steady flow, draw the imaginary envelope around the medium to be analyzed both before and after the process.
3. Indicate the forms of energy entering or leaving the apparatus with the medium or mediums involved, in a steady-flow process, or the forms of energy associated with the medium or mediums at the beginning and also at the end of the process for a nonflow or nonsteady-flow process. Also, indicate the forms of energy that enter or leave the medium during the process.
4. Draw P-V and T-S diagrams of the process. Work and heat terms may be evaluated by areas on these diagrams in all ideal or reversible* processes.
5. Write the Energy Equation for the process.
6. Evaluate the known energy terms and solve the Energy Equation for the unknown value. The evaluation of the various terms in the Energy Equation and its solution depend on a knowledge of the thermo-

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* In general, only ideal or reversible processes are dealt with in the first six chapters. These terms are used here and elsewhere, although not defined until Chap. VII, merely to warn the student that there are friction or irreversible processes to be studied later for which the usual areas on the P-V and T-S diagrams do not represent the work or heat items, respectively.

dynamic properties of the medium or mediums involved. These are developed and applied to solutions in the following chapters.

Negligibility of Energy Terms.—In many processes some form or forms of energy are present but are of small value. These may be neglected only if their elimination does not seriously change the result of the analysis, and this depends principally on the process. A difference in elevation of 77.8 ft between the entering and the leaving fluid in a steady-flow process indicates a difference of 77.8 ft-lb or 0.1 Btu/lb of medium flowing. This would be negligible if the process in question indicated a solution for work or any other energy term amounting to 100 Btu, since the error in neglecting the potential energy terms would be 0.1 per cent. However, for the case of a falling body the difference in the potential energy terms is the maximum possible kinetic energy obtainable, and consequently the potential energy terms could not be neglected.

All steady-flow processes have kinetic energy of the fluid associated with them. In many cases these terms may be neglected. However, the same criterion as indicated in the foregoing should be applied in determining the negligibility of these as well as any other terms.

In general, each energy term, for which data are available, should be evaluated before elimination from the Energy Equation.

EXERCISES

Analyze the following processes by drawing diagrammatic sketches of the apparatus involved and P-V and T-S diagrams of the process. Indicate the areas representing work and heat-transfer values where possible. Indicate the energy terms that are omitted because of negligibility of amount.

1. A body is released from an airplane in flight. Write the Energy Equation (*a*) for the body beginning with the instant of release from the plane and ending just before reaching the earth. Consider the air that is affected by the falling body. (*b*) Also for the case when the body has come to rest on the earth for the end of the process.

2. A closed steel cylinder is filled with a gas at atmospheric temperature. Electrical energy is supplied at a constant rate to a resistance element in the gas, and the temperature of the gas rises to an equilibrium temperature. Write the Energy Equation for the gas (*a*) for the period of time during which the temperature is rising, (*b*) for a period of time after the equilibrium temperature is attained (1) with current flowing to maintain equilibrium, (2) with circuit open.

3. An electric heater is used to heat the air in an engine cylinder. Write the Energy Equation for the heating of the air from a low to the desired temperature while the piston moves and permits an increase in volume.

4. A gaseous medium at high pressure is in an engine cylinder. Both the gas and the cylinder are at atmospheric temperature. The piston is allowed to move and the gas is expanded to a larger volume. Write the Energy Equation for the gas for (*a*) an extremely rapid expansion, (*b*) a comparatively slow expansion, (*c*) an extremely slow expansion.

5. A throttling device is a restriction to flow. A "cracked" valve (one that is opened only a small amount) is a throttling valve. The area of the valve opening is small compared to the pipe size. Flow is steady, and the process is to be analyzed from a point appreciably ahead to a point appreciably beyond the valve.

6. An orifice or nozzle is a device through which a medium flows from high to low pressures. It might also be termed a throttling device. However, the nozzle is smooth and streamlined to facilitate the development of the highest fluid velocity. Write the Energy Equation for steady flow beginning with a point appreciably ahead of the nozzle to a point at the low-pressure end of the nozzle.

7. Gas flows steadily through a long pipe line exposed to the atmosphere. Write the Energy Equation for the gas flowing through it.

8. Steam at high pressure and temperature flows steadily to a steam turbine. The steam leaves the turbine at a fairly high velocity after reacting on and doing work on the turbine blades. Write the Energy Equation for the steam starting with a point in the pipe line ahead of the turbine and ending with a point in the exhaust connection.

9. A steel chamber is divided into two parts by a thin metallic diaphragm. On one side is a perfect vacuum; on the other side is a definite amount of high-pressure steam. The diaphragm ruptures, and the steam fills the entire chamber. Write the Energy Equation for the process, assuming no heat transfer to or from the chamber.

10. An electric-light bulb is perfectly evacuated. A crack develops and air flows into the bulb. Write the Energy Equation for the following cases: (*a*) if the air fills the bulb very quickly, (*b*) if the air flows very slowly into the bulb.

11. A bomb or constant-volume calorimeter is used to determine the calorific value of a fuel. Oxygen and the fuel react in the bomb, and the heat that flows to the water bath around the bomb is called the heat value at constant volume. This is evaluated on the assumption that the products of reaction are cooled to the temperature of the fuel and oxygen before the reaction. Write the Energy Equation for the fuel-oxygen mixture and products of reaction in the process.

12. A constant-pressure steady-flow process is used for gas calorimetry. The gas and air flow into the calorimeter, combustion occurs, and the products of reaction are cooled to the initial temperature which is usually atmospheric. A steady flow of water through the calorimeter absorbs the heat of combustion. Write the Energy Equation for the fuel, oxygen, and products of combustion involved in the process; for the cooling water; and, for all mediums.

13. Gas and air flow into a Bunsen burner. The mixture is ignited and flows away from the burner at a high temperature. Analyze the process by writing the Energy Equation.

14. Air and gasoline flow steadily to a multicylinder engine, react, do work on the engine piston, and then leave as products of combustion. Analyze the engine process by assuming that an envelope surrounds the engine and cuts the various pipe lines and engine shaft. Then write the Energy Equation.

15. A combustible mixture of gasoline and air is in an engine cylinder. The volume of the mixture at the end of the compression process is one-fifth of the volume at the beginning of this process. Ignition occurs at a piston position of 80 per cent of the compression stroke. Combustion has attained an equilibrium at a piston position of 10 per cent of the expansion stroke. Write the Energy Equation only for the process from ignition to the combustion equilibrium.

16. A gun is mounted to fire a projectile at an angle of elevation. Write the Energy Equation for the powder, the projectile, the gun, the air, and all together beginning with the time immediately preceding the firing of the gun and ending with the projectile (*a*) at the end of the gun barrel, (*b*) at the top of its trajectory, (*c*) buried in the earth at the end of its flight.

17. Steam flows at a moderate velocity from a steam turbine into a condenser. The pressure in the condenser is considerably below atmospheric. Cooling water flows through tubes in the condenser and condenses the steam contacting the other side of the tubes. A pump is required to remove the condensed steam from the condenser. Write the Energy Equation for the steam and cooling water.

18. Write the Energy Equation for a piston in a cylinder for the following cases: (*a*) during the compression process only for an air compressor, (*b*) during the expansion process only for an automobile engine, (*c*) during the expansion process of air which initially is at high pressure and atmospheric temperature.

19. Write the Energy Equation for a self-contained household electric refrigerator, for the air in a closed room containing the refrigerator, and for both combined.

20. The fire has been dumped from a portable steam boiler which has been left standing in the atmosphere. Write the Energy Equation for the boiler and its contents from the dumping of the fire until the boiler cools to atmospheric temperature.

CHAPTER IV

PROPERTIES OF MEDIUMS

Energy Terms Dependent on Mediums.—The solution of most thermodynamic processes necessitates the formulation of the Energy Equation for the given process and the substitution of quantitative values for the energy terms involved. Obviously, one of the energy terms can be determined from the solution of the Energy Equation when all the other terms are known.

The method of evaluating some of the various forms of work as a force times the distance through which the force acts is illustrated for various processes in Chap. II. Both potential-energy and kinetic-energy values are based on this work concept, the former depending on the position and the latter on the velocity of the medium as a whole.

The chemical energy associated with the change in electronic, atomic, or molecular arrangement is usually determined from the calorimeter process. This form of energy depends on the mediums and the nature of the change involved.

The heat transferred can in some cases be evaluated from the effect on the medium receiving or rejecting the heat. This is possible when the medium involved is finite in amount and the heat transferred produces an appreciable temperature effect such as occurs with constant-volume or constant-pressure changes; or, in a change of state from solid to liquid, etc., at constant pressure and temperature. Also, the heat transfer may be evaluated from the *T-S* diagram for ideal cases. In other cases the usual method of evaluating heat transfer from heat-transfer coefficients, temperature difference between the medium and the surrounding or containing surface, the area through which heat transfer occurs, and the elapsed time must be used. In most problems of elementary thermodynamics the amount of heat transferred is given or is evaluated from the Energy Equation. In all actual cases, however, the heat transfer must be either given or evaluated by one of the methods indicated.

It has been noted that internal energy of gases and vapors is now evaluated by the use of the spectroscope and statistical mechanics. However, the heating method is used for the evaluation of internal energy of solids and liquids, as well as the internal-energy change during a change of state from solid to liquid or liquid to vapor, or vice versa.

Evaluation of Properties of Mediums.—The pressure (or temperature) and volume of a given quantity of medium uniquely indicate the condition of the medium. When H_2O exerts a pressure of 14.696 lb/in.^{2} and 1 lb has a volume of 26.80 ft^3, the H_2O is vapor at 212 F,* and any transfer of heat in or out will result in a rise in temperature or a condensation of some vapor, respectively, if held at constant pressure. Thus, at each condition of pressure (or temperature) and volume for a given quantity of medium there is associated with this condition a definite molecular condition or internal energy.

The evaluation of the internal energy of a medium could theoretically be determined by heating the medium from a condition at which $U_1 = 0$ to the desired condition and evaluating U_2 from the various energy effects. However, this would involve a number of difficulties† so that internal energy is evaluated above an arbitrary datum plane. The Energy Equation for the constant-volume heating process is

$$U_1 + Q_{\text{in}} = U_2 \tag{1}$$

from which it is seen that the heat added is the increase in internal energy for the process. This process would be most desirable if it were possible to maintain the volume constant. This is practically impossible and has led to the adoption of the steady-flow heating process for the evaluation of internal energy. The Energy Equation for the process is

$$U_1 + P_1V_1 + Q_{\text{in}} = U_2 + P_2V_2 \tag{2}$$

or

$$H_1 + Q_{\text{in}} = H_2 \tag{3}$$

Thus, the increase in enthalpy is evaluated directly from the heat added during this process, and the internal energy is evaluated therefrom. Tables of properties of mediums contain pressure, temperature, volume, enthalpy, and entropy data for a unit quantity of medium. In some cases internal-energy values are included but, in any case, the internal-energy value can be determined from the relation

$$U = H - PV \tag{4}$$

Usually an arbitrary datum condition is chosen above and below which

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* See H_2O tables in Appendix. The symbol H_2O is used here and elsewhere instead of ice, water, steam, and gaseous H_2O. Thus, no clue is given by the symbol as to the state of the medium, which must be determined by an examination of the conditions, which are assumed to be those of equilibrium.

† See footnote, p. 45.

H, *U*, and *S* are determined. (See the tables of properties of various mediums in the Appendix.)

Heating a Medium at Constant Pressure.—When heat is added to a medium in the solid state, in the presence of its vapor only, and under a low constant pressure, the temperature of the medium rises until the sublimation temperature is reached. Further addition of heat to the medium under the same conditions causes the solid to change into a vapor at this sublimation temperature. The solid disappears and the volume increases considerably during this process, which is one of constant pressure and temperature. A further addition of heat to the medium now in the vapor state, while being held at the same constant pressure, results in an increase in temperature above the sublimation temperature, and the vapor becomes superheated.

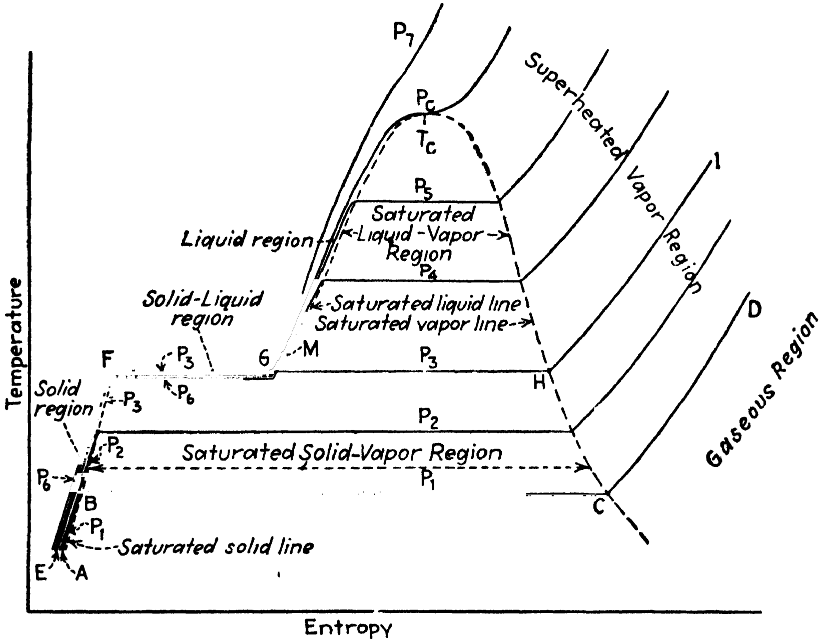

FIG. 25.—*T-S* diagram of constant-pressure heating curves for H_2O. (Not to scale.)

The entropy changes for the three parts of the foregoing heating process can be computed* and the process plotted on a temperature-entropy diagram (see path *ABCD*, Fig. 25). The path *AB* represents the heating of the solid, *BC* the sublimation of the solid to vapor, and *CD* the superheating of the vapor. The heating process at a higher pressure (P_2)

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* See the section on Heat Diagrams and Entropy in Chap. II.

results in a similar path but with slightly higher temperatures at given entropies along the heating path for the solid, a higher sublimation temperature, and also higher temperatures at given entropies along the path for the superheated vapor. A pressure (P_3), higher than pressure P_2, results in path *EFGHI*, of which *EF* is similar to *AB*, but from *F* to *G* the solid is changed to a liquid and from *G* to *H* is changed from liquid to vapor. Path *HI* is similar to the superheating paths at the lower pressures.

Most mediums undergo a change in volume in changing from the liquid to the solid state, or vice versa. Liquid H_2O increases in volume while changing to solid H_2O, which is commonly termed *ice*. An increase in pressure tends to prevent this increase in volume of water upon solidifying and consequently lowers the freezing temperature. Thus the path for P_4, which is a higher pressure, has a slightly lower melting temperature than P_3. Addition of heat to the liquid at the melting temperature results in a temperature rise to the boiling point, corresponding to the pressure, at which temperature vaporization occurs and beyond which superheating takes place as in all the previous cases. The heating of H_2O at a higher pressure P_5 results in higher temperatures in the solid region and a lower melting temperature than for P_4. The P_5 line intersects the P_4 line at *M* the minimum-volume temperature,* and has a higher boiling temperature.

* This occurs at about 39.2 F for H_2O at moderate pressures. The following Maxwell relation [Eq. (26) Appendix] may be used to prove the crossing of the different pressure lines:

$$\left(\frac{\delta S}{\delta P}\right)_T = -\left(\frac{\delta V}{\delta T}\right)_P$$

at any given temperature becomes

$$S_2 - S_1 = -\int_{P_1}^{P_2}\left(\frac{\delta V}{\delta T}\right)_P dP$$

At the minimum volume, $(\delta V/\delta T)_P = 0$, and, consequently, there is no difference in entropy of the two pressure lines at this temperature. Hence they must cross at this temperature.

Bridgman has shown that the minimum-volume temperature is lowered with an increase in pressure. [See *Proc. Am. Acad. Arts Sci.*, **47**, 13, 441–558 (1912).]

If absolute entropy is desired, the heating process is assumed to start at absolute zero temperature with the medium in the perfectly crystalline state. The entropy at this condition is assumed to be zero according to the *Third Law of Thermodynamics.* Usually specific heat data are not available below about 22° R, and the entropy change is estimated from zero to this temperature from Debye's Equation (see M. W. Zemansky, "Heat and Thermodynamics," p. 239, McGraw-Hill Book Company, Inc., New York, 1937) or the mean specific heat for this temperature range is assumed to be one-third of the specific heat at 22°R.

In some cases the solid undergoes a transition at some higher temperature to a second form of solid, and further heating results in the changes indicated in the text. Thus, The path for the critical pressure (P_c), at and above which the constant temperature vaporization or condensation process will not occur, is similar to the two preceding paths, there being merely a point of inflection at the critical temperature (T_c). Higher pressures result in paths similar to that for P_c but with less inflection than that of the critical-pressure path.

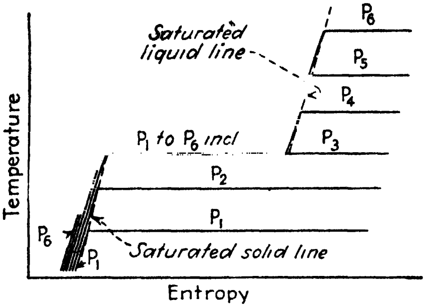

FIG. 26.—T-S diagram for mediums having no volume change from solid to liquid states, and an increase in volume of solid and liquid with an increase in temperature.

Critical pressure and temperature data are given in Table IV, Appendix.

T-S Diagram for Mediums with Characteristics Other Than Those of H_2O.—Mediums that do not have a minimum liquid volume will not have the constant-pressure lines crossing as at M in Fig. 25. Also, pressure will not have any effect on the melting temperature if the volume of the solid is the same as the volume of the liquid at this temperature. Finally, the high-pressure lines will be above the low-pressure ones in the case of both solid and liquid if the volume increases with an increase in temperature under constant-pressure conditions. Mediums with these characteristics would have constant-pressure heating paths similar to those in Fig. 26.

Mediums that have the foregoing characteristics with the exception of having a decrease in volume upon solidifying (such as CO_2) will have the melting temperature increased with an increase in pressure (Fig. 27).

Saturation Line.—A line connecting all the points indicating the beginning of vaporization of the solid at the various pressures is called the *saturated-solid line.* A definite pressure is associated with each point on this curve, the temperature being the sublimation temperature for that pressure. A process following this path would not have any of the three

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the absolute value of entropy of a medium, which undergoes solid transition, melting, and evaporation may be evaluated from the following equation, the integrals being obtained graphically from plots of c_P/T vs. T:

$$S = \int_0^{22} c_P(\text{solid}_1)\frac{dT}{T} + \int_{22}^{T_t} c_P(\text{solid}_1)\frac{dT}{T} + \frac{H_t}{T_t} + \int_{T_t}^{T_m} c_P(\text{solid}_2)\frac{dT}{T}$$

$$+ \frac{H_m}{T_m} + \int_{T_m}^{T_{fg}} c_P(\text{liquid})\frac{dT}{T} + \frac{H_{fg}}{T_{fg}} + \int_{T_{fg}}^{T} c_P(\text{gas})\frac{dT}{T}$$

where subscripts t, m, and fg indicate *solid transition*, *melting*, and *evaporation*, respectively.

coordinates P, V, and T held constant. Also the relations between the coordinates for this line are

$$P = f(T) \qquad \text{and} \qquad V = f(P \text{ or } T)$$

The region occupied by constant-pressure lines to the left of the saturated-solid line is considerably expanded in area in Figs. 25 to 27, for the pressures. usually encountered, and is called the *solid*, *subcooled*, or *compressed-solid* region.

The locus of all the points indicating the beginning of vaporization of the liquid at the various pressures is called the *saturated-liquid line.* The pressures at the various points on this curve are also functions of the temperatures, and the liquid volumes are functions of the pressure or the temperature. The region occupied by constant-pressure lines to the left of the saturated-liquid line is also expanded in area in Figs. 25 to 27, and is called the *liquid*, *subcooled*, or *compressed-liquid* region.

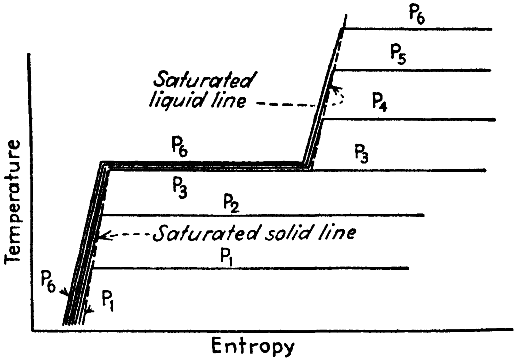

FIG. 27.—T-S diagram for mediums having an increase in volume from solid to liquid states, and an increase in volume of solid and liquid with an increase in temperature.

The locus of all points indicating the end of the vaporization or sublimation processes is called the *saturated-vapor line.* The saturated-liquid and -vapor lines are usually joined at the critical temperature by a smooth curve (Fig. 25), while the saturated-solid and -liquid lines are joined by the one melting line at the temperature and corresponding pressure at which the solid changes first to liquid and then to vapor upon the transfer of heat to it.

Properties of Solids and Liquids.—The solid and liquid regions (Figs. 25 to 27) are similar, except for the peculiar characteristic of H_2O in the small range from 32 to 39.2 F. Consequently, the treatment of the properties of the solid state will be similar to that of the liquid state for which considerable data are available in the case of H_2O. Table V, Appendix, contains the properties of H_2O as prepared by Keenan and Keyes. Values of the specific volume V, internal energy U, enthalpy H, and entropy S are given for various temperatures both along the saturated-liquid line and along various constant-pressure lines.

Example.—Determine the specific volume, enthalpy, and entropy of H_2O at 1,000 lb/in.^{2} pr and 500 F. Also for the saturated condition at 1,000 lb pressure. On the left side of Table V, Appendix, the pressure of 1,000 lb will be found with the saturation temperature (544.61) below it. To the right of this and below the 500 F temperature indicated at the top of the table will be found

$$V = 0.020368 \text{ ft}^3 \qquad H = 487.68 \text{ Btu}$$

and

$$S = 0.68730 \text{ Btu/°R}$$

The data for saturated H_2O are given at the top for temperatures and at the right side for pressures. Consequently, at the right side, opposite the 1,000 lb on the left, will be found

$$V = 0.0216 \text{ ft}^3 \quad H = 542.4 \text{ Btu} \quad \text{and} \quad S = 0.7430$$

The small differences in position of the saturated-liquid line and the various pressure lines, as indicated by the entropy values at any temperature, has led to the assumption in some cases that the saturated-liquid line and the various pressure lines up to their saturation temperatures are identical in position and values. Under some conditions this assumption is justifiable since little error is introduced. However, it may result in appreciable error for certain pressure and temperature ranges, as well as for certain substances.*

Example.—H_2O is heated under a constant pressure of 2,000 lb/in.^{2} from 100 to 600 F. Determine the difference between the heat added per pound of medium and the increase in enthalpy along the saturation curve between the two temperatures given. From Table V, Appendix,

At 600 F and 2,000 lb/in.^{2} $\qquad H_2 = 614.5$ Btu/lb
At 100 F and 2,000 lb/in.^{2} $\qquad H_1 = 73.3$ Btu/lb

For a constant-pressure process, $Q_{in} = H_2 - H_1 = 541.2$ Btu/lb

At 600 F and saturation pressure $\qquad H_2 = 617.0$ Btu/lb
At 100 F and saturation pressure $\qquad H_1 = 68.0$ Btu/lb

For a saturated liquid process $\qquad H_2 - H_1 = 549.0$ Btu/lb

The two methods show a difference of 7.8 Btu/lb, the incorrect method introducing an error of more than 1 per cent.

The enthalpy of the compressed liquid or solid *cannot be estimated* by any simple assumption such as the following:

---

* See Chart C, Appendix.

In the solid or liquid region,

$$H = U + PV \tag{1}$$

At the same temperature and at the saturated solid or liquid line

$$H_f = U_f + (PV)_f \tag{2}$$

Now, assuming $U = U_f$, $V = V_f$, and combining Eqs. (1) and (2)

$$H = H_f + (P - P_f)V_f \tag{3}$$

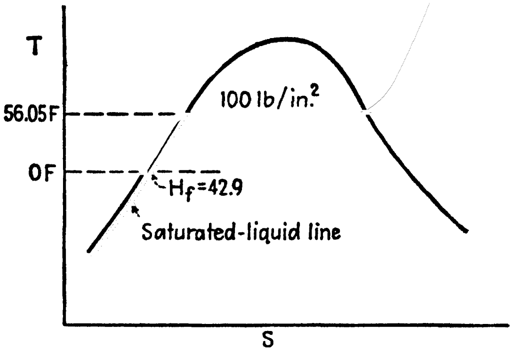

FIG. 28.—*T-S* diagram for ammonia indicating approximation for properties in the subcooled region.

This indicates that H is greater than H_f if P is greater than P_f and, consequently, H lines in the solid or liquid region on the *T-S* diagram should slope downward to the left of the saturated line. An inspection of Chart C for carbon dioxide indicates this is true for only a small part of the liquid region and very inaccurate elsewhere. Thus, if energy values for the compressed liquid and solid region are not available, the saturated values at the same temperature should be used rather than attempting to evaluate H in the compressed region by the foregoing inaccurate method.

Applying Eq. (18), Appendix, to a constant-temperature process results in

$$\left(\frac{\delta H}{\delta P}\right)_T = V + T\left(\frac{\delta S}{\delta P}\right)_T \tag{4}$$

Combining with Eq. (26), Appendix, results in

$$\left(\frac{\delta H}{\delta P}\right)_T = V - T\left(\frac{\delta V}{\delta P}\right)_P \tag{5}$$

Thus, the relative value of the two terms on the right side of this equation indicates whether H increases or decreases along any given constant-temperature line.

Example.—Determine the value to be used for H for ammonia at 100 lb/in.^{2} abs and 0 F.

The boiling temperature for this pressure is 56.05 F (Table X, Appendix). The *T-S* diagram (Fig. 28) indicates that the condition in question is very much nearer the saturated liquid at 0 F than the saturated liquid at 100 lb/in.^{2}

Hence, a value of H_f of 42.9 Btu/lb (Table IX, Appendix) at T = 0 F should be used since no data are available for the compressed-liquid region for ammonia.

Properties of Saturated Mediums.—Tables of properties of saturated liquid and vapor usually contain values for the three coordinates P, V, and T, and values for internal energy U, enthalpy H, and entropy S, for both the saturated liquid and vapor, as well as changes in these properties between the two saturation lines. This applies also to tables of properties dealing with the saturated solid-vapor region. The *values* of the various properties *are* either *on the saturated-liquid or saturated-solid line, on the saturated-vapor line, or represent the change in that property between the two lines at a given temperature,* the location being indicated by subscripts f or i, g, and ig or fg, respectively.

Example.—Determine the volume, enthalpy, internal energy, and entropy of saturated H_2O at both the liquid and vapor lines, at 700 lb/in.^{2} abs pr.

Referring to Table VII, Appendix, which is the H_2O saturated liquid-vapor table based on pressure, the following values per pound of medium will be found for 700 lb pr:

V	H	U	S
Saturated liquid			
0.0205 ft^3	491.5 Btu	488.8 Btu	0.6925 Btu/°R
Saturated vapor			
0.6554 ft^3	1201.2 Btu	1116.3 Btu	1.4296 Btu/°R

In the second column in Table VII will be found the saturation temperature of 503.10 F for 700 lb pr. The temperature nearest this in Table VI, Appendix, is 500 F for which almost the same data as above will be found.

When vaporization is incomplete, the liquid remaining is saturated and its condition is indicated by a point on the saturated-liquid line while the portion that is vaporized is saturated and its condition is indicated by a point on the saturated-vapor line, both at the same temperature and pressure. It is customary to represent this condition by a point on the line between these two such that its location indicates the weight fraction or per cent of the medium that is vaporized. Since the vaporization process is one of constant temperature, the areas beneath equal increments of the line representing this process, on the T-S diagram, represent equal increments of the various properties. Thus, each vaporization line may be divided into any number of equal parts, and each part will represent the same proportionate part of the change of any property. The symbol x is used to represent the *part of the vaporization process* that has been completed, and is termed the *quality* of the mixture of liquid and vapor, or solid and vapor.

At any quality x, the volume of the vapor is xV_g, and the volume of the liquid is $(1-x)V_f$. The total volume per unit quantity is

$$V_x = (1-x)V_f + xV_g, \qquad \text{or} \qquad V_x = V_f + xV_{fg} \tag{1}$$

Likewise,

$$U_x = (1-x)U_f + xU_g, \qquad \text{or} \qquad U_x = U_f + xU_{fg} \tag{2}$$

$$H_x = (1-x)H_f + xH_g, \qquad \text{or} \qquad H_x = H_f + xH_{fg} \tag{3}$$

$$S_x = (1-x)S_f + xS_g, \qquad \text{or} \qquad S_x = S_f + xS_{fg} \tag{4}$$

Adding and subtracting V_{fg} to and from the right side of Eq. (1),

$$V_x = V_g - (1-x)V_{fg} \tag{5}$$

Likewise, similar expressions may be written for U_x, H_x, and S_x.*

Example.—A pound of H_2O is 50 per cent evaporated in the presence of its own vapor at a pressure of 100 lb/in.^{2} abs. Determine the internal energy of the mixture.

From Table VII, Appendix, at 100 lb/in.^{2}

$$U_f = 298.08 \text{ Btu} \qquad U_{fg} = 807.1 \text{ Btu} \qquad U_g = 1105.2 \text{ Btu}$$

Using the first method,

$$\begin{aligned} U_x &= U_f + xU_{fg} \\ &= 298.08 + 0.5 \times 807.1 = 701.6 \text{ Btu} \end{aligned}$$

Using the second method,

$$\begin{aligned} U_x &= U_g - (1 - x)U_{fg} \\ &= 1105.2 - (1 - 0.5)807.1 = 701.6 \text{ Btu} \end{aligned}$$

Critical Data.—The *critical temperature* is the temperature below which a medium can be condensed, *i.e.*, a gas can be compressed to a saturated vapor and then be condensed to a liquid at constant pressure. Above the critical temperature a medium cannot be made to undergo the foregoing condensation process, *i.e.*, there is no apparent change of state as a medium is compressed at constant temperature from the gaseous state to a condition of very high pressure.

The *critical pressure* is the pressure below which a medium can be evaporated from a liquid to a saturated vapor, etc., during constant-pressure heating. A compressed liquid when heated at constant pressure above the critical pressure does not undergo an apparent change of state as the temperature is increased from below to above the critical temperature (see Heating a Medium at Constant Pressure, page 44).

---

* These expressions should be used when the quality of the medium is higher than 0.5, while the other form should be used when the quality is less than 0.5 in order to obtain the more accurate results with slide-rule computations.

The foregoing definitions indicate that at the critical temperature and pressure the specific volumes of saturated liquid, V_f, and saturated vapor, V_g, are identical. This volume is termed the *critical volume.*

Critical temperature, pressure, and volume data are given in Table IV, Appendix.

Properties of Superheated Mediums.—Tables of properties of superheated mediums usually contain values of specific volume, V, enthalpy, H, and entropy, S, at various temperatures for various pressures. Values of internal energy, U, can be obtained from the relation

$$U = H - PV \qquad (1)^*$$

The difference in temperature between any superheated condition and the saturation temperature for the same pressure is called the *superheat.* Thus if H_2O is at 312 F and atmospheric pressure, the H_2O is superheated 100 F, since 212 F is the saturation temperature for H_2O at atmospheric pressure.

Example.—H_2O at 200 lb/in.^{2} abs pr is superheated 519.21 F. Determine the temperature of the H_2O and values for U, H, V, and S.

From Table VIII, Appendix, the saturation temperature for 200 lb pr is 381.79 F. Adding 519.21 F results in a temperature of 900 F. From the same table for 200 lb pr and 900 F, $U = 1{,}328.1$, $H = 1{,}476.2$, $V = 4.002$, and $S = 1.8048$.

The Gaseous Region.—Such mediums as helium, hydrogen, oxygen, nitrogen, air, carbon monoxide, and carbon dioxide, under usual atmospheric pressure and temperature conditions are termed *gases.* Under this condition all these mediums are highly superheated at moderately low pressure.

Joule's classical free-expansion experiment in which gas at high pressure in one chamber (Fig. 29) was allowed to flow into another chamber having little or no gas in it to begin with, resulted in heat transfer from the water bath into chamber A, and heat transfer out of chamber B into the water bath. However, the heat-transfer effects were practically equal and the final equilibrium temperature of the water bath and the medium was the same as before the expansion process. During this process no heat transfer

---

* If P is in lb/in.^{2}, V in ft^3/lb, and U and H are in Btu,

$$U = H - \frac{144PV}{778} = H - 0.1852PV = H - \frac{PV}{5.403}$$

or work passed through an imaginary envelope around the water bath. Hence the Energy Equation for the process is

$$U_1 = U_2 \tag{1}$$

The condition and consequently the internal energy of the water bath was the same before and after the process. Thus, it was concluded that the internal energy of the gaseous medium did not change. Since pressure and specific volume of the gaseous medium both change, while internal energy and temperature do not, it followed that the internal energy of a medium in the gaseous state is a function of the temperature only.

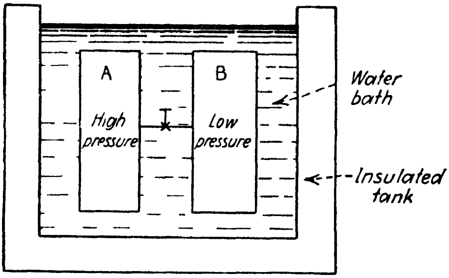

FIG. 29.—Joule's free-expansion apparatus.

More refined experiments of this nature resulted in appreciable temperature change but, as the pressure of any superheated medium approaches zero, these experiments indicate that the internal energy of the medium approaches a function of the temperature only. Also as the pressure of a superheated medium approaches zero the product of P and V approaches a constant that is proportional to the absolute temperature.

Since,

$$H = U + PV \tag{2}$$

the enthalpy of a medium in the perfect gaseous state is also a function of the temperature only.

Thus, the *perfect-gas region,* for any medium, is defined on any diagram as *that region in which the enthalpy and internal-energy lines are parallel to temperature lines,* and it is incorrect to use perfect-gas relationships except when this condition is closely approached. In such cases the use of these relationships introduces a negligible error.

Properties of Mediums in the Perfect-gas State.—The specific volume of a medium in the perfect-gas state, like that of the superheated vapor state, is a function of both pressure and temperature. Boyle's experiments showed that with constant temperature the absolute pressures varied inversely with the volumes. Thus,

$$P_1V_1 = P_2V_2 = PV = \text{const} \quad (1)$$

Charles' experiments showed that, with constant pressure, the volumes varied directly with the absolute temperatures. Thus,

$$V_1/V_2 = T_1/T_2 \quad (2)$$

Also, holding the volumes constant, he found that

$$P_1/P_2 = T_1/T_2 \quad (3)$$

The *Equation of State* for a perfect gas, relating the three coordinates P, V, and T, can be obtained from these three relationships. It is

$$P_1V_1/T_1 = P_2V_2/T_2 = PV/T = \text{const} \quad (4)$$

or

$$PV = RT^* \quad (5)$$

Example.—Derive the Equation of State for mediums in the perfect-gas state. Assume that a constant-temperature process occurs from the initial condition represented by P_1, V_1, and T_1 to a second condition of P_2, V_1', and T_1. Thus

$$P_1V_1 = P_2V_1'$$

Now assume a constant-pressure process changing the conditions from the second condition above to a third condition of P_2, V_2, and T_2. Then,

$$V_1'/V_2 = T_1/T_2$$

Combining these two relations and eliminating V_1', result in

$$P_1V_1/T_1 = P_2V_2/T_2 = \text{etc.}$$

Avogadro has shown that quantities of gaseous mediums proportional to their respective molecular weights have the same volumes at the same pressure and temperature. Thus, 32 lb of O_2, 28 lb of N_2, 44 lb of CO_2, etc., will each occupy the same volume at the same pressure and temperature. This quantity of material, the molecular weight in pounds, is termed a *mole*. It follows that the gas constant R of the Equation of State is the same for all mediums in the perfect-gas state when the quantity of material dealt with is in terms of moles.

The value of R is 1,545 ft-lb/(mole × °R) or 1.986 Btu/(mole × °R). Also, since M moles will have M times the volume of 1 mole, the Equation of State for M moles of a perfect gas is

$$PV = MRT \quad (6)$$

---

* This expression can be derived from the kinetic theory of perfect gases. See any physics text.

Example.—Determine the volume of 1 mole and 1 lb of nitrogen at a pressure of 14.7 lb/in.^{2} and a temperature of 32 F.

$$\begin{aligned} V &= MRT/P \\ &= \frac{1 \text{ mole} \times 1{,}545 \text{ ft-lb/(mole} \times {}^\circ\text{R)} \times 492^\circ\text{R}}{14.7 \text{ lb/in.}^2 \times 144 \text{ in.}^2/\text{ft}^2} \\ &= 358.8 \text{ ft}^3/\text{mole} \end{aligned}$$

The molecular weight of nitrogen is 28. Hence, 1 mole of nitrogen is equivalent to 28 lb and the volume of 1 lb will be

$$\frac{358.8 \text{ ft}^3/\text{mole}}{28 \text{ lb/mole}} = 12.81 \text{ ft}^3/\text{lb}$$

The *internal energy* and *specific heats* of mediums in the perfect-gas state are functions of the temperature and are related through the Energy Equation for a nonflow constant-volume heating process. For this process

$$U_1 + Q_{\text{in}} = U_2 \tag{7}$$

Also,

$$Q_{\text{in}} = \int_{T_1}^{T_2} c_V \, dT \tag{8}$$

Hence,

$$U_2 - U_1 = \int_{T_1}^{T_2} c_V \, dT \tag{9}$$

A constant value may be substituted for c_V for small temperature ranges, or a variable specific-heat equation for large temperature ranges. Values of internal energy, based on spectroscopic analysis and statistical mechanics, have been computed for various gases (Table XIX, Appendix). These data eliminate the necessity of using the specific-heat relationships in the solution of many problems dealing with gaseous mediums.

The *enthalpy* of mediums in the gaseous state may be obtained from the nonflow constant-pressure heating process. Thus, from Eq. (17), page 38,

$$H_1 + Q_{\text{in}} = H_2 \tag{10}$$

Also,

$$Q_{\text{in}} = \int_{T_1}^{T_2} c_P \, dT \tag{11}$$

Hence,

$$H_2 - H_1 = \int_{T_1}^{T_2} c_P \, dT \tag{12}$$

Values of enthalpy for gaseous mediums may be obtained by adding corresponding values of U and PV listed in Table XIX, Appendix, instead of using specific-heat data.

The *entropy change* of a perfect gas may be obtained from the Energy Equation for a nonflow heating process. Thus,

$$U_1 + Q_{in} = U_2 + W_{out} \tag{13}$$

Also,
$$Q_{in} = \int_{S_1}^{S_2} T\,dS \tag{14}$$

and
$$W_{out} = \int_{V_1}^{V_2} P\,dV \tag{15}$$

both for ideal cases.

Combining these equations with Eq. (9) results in

$$dS = c_V\,dT/T + P\,dV/T \tag{16}$$

But since $P/T = R/V$ for 1 mole of a perfect gas,

$$S_2 - S_1 = \int_{T_1}^{T_2} c_V \frac{dT}{T} + \int_{V_1}^{V_2} R\frac{dV}{V} \tag{17}$$

or
$$S = \int_{T_0}^{T} c_V \frac{dT}{T} + R \ln \frac{V}{V_0} + S_{0_{T,V}} \tag{18}$$

in which the subscript 0 indicates the datum condition.

Differentiating $PV = RT$ and dividing by T,

$$P\,dV/T + V\,dP/T = R\,dT/T \tag{19}$$

Eliminating $P\,dV/T$ between Eqs. (16) and (19),

$$dS = (c_V + R)\frac{dT}{T} - \frac{V\,dP}{T} \tag{20}$$

For the constant-pressure heating process

$$Q_{in} = \int c_P\,dT = \int dH = \int d(U + RT) = \int c_V\,dT + \int R\,dT \tag{21}$$

from which
$$c_P = c_V + R \tag{22}$$

Combining Eqs. (20) and (22) with the Equation of State results in

$$dS = c_P\frac{dT}{T} - R\frac{dP}{P} \tag{23}$$

or
$$S_2 - S_1 = \int_{T_1}^{T_2} c_P\frac{dT}{T} - \int_{P_1}^{P_2} R\frac{dP}{P} \tag{24}$$

and
$$S = \int_{T_0}^{T} c_P\frac{dT}{T} - R \ln \frac{P}{P_0} + S_{0_{T,P}} \tag{25}$$

By equating (16) and (23) and simplifying, it can be seen that

$$dT/T = dP/P + dV/V \tag{26}$$

which, when substituted into either Eq. (17) or (24), results in the third expression for entropy, namely,

$$S_2 - S_1 = \int_{P_1}^{P_2} c_V \frac{dP}{P} + \int_{V_1}^{V_2} c_P \frac{dV}{V} \tag{27}$$

or

$$S = c_V \ln \frac{P}{P_0} + c_P \ln \frac{V}{V_0} + S_{0_{P,V}} \tag{28}$$

if c_V and c_P are constant.

It should be noted that each expression for entropy is a function of a pair of coordinates (T,V), (T,P), and (P,V), there being three pairs for the three coordinates. Also, the value of the constant of integration S_0 depends on the coordinates defining it and the lower limit for the various integrals.

Example.—Determine the entropy change for 1 mole of air in having its pressure doubled and its volume tripled. Assume that c_P for 1 mole of air is constant at 6.9 Btu/°R.

$$S_2 - S_1 = \int_{P_1}^{P_2} c_V \frac{dP}{P} + \int_{V_1}^{V_2} c_P \frac{dV}{V} \tag{27}$$

$$\begin{aligned} R &= 1{,}545 \text{ ft-lb/(mole} \times {}^\circ\text{R)} = 1.986 \text{ Btu/(mole} \times {}^\circ\text{R)} \\ S_2 - S_1 &= (6.9 - 1.986) \ln 2 + 6.9 \ln 3 \\ &= 10.99 \text{ Btu/(mole} \times {}^\circ\text{R)} \end{aligned}$$

Example.—Determine the entropy change in the preceding example by using Eq. (24).

$$S_2 - S_1 = c_P \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

A value for T_2/T_1 can be obtained from the Equation of State for gaseous mediums. Thus,

$$\begin{aligned} T_2/T_1 &= P_2V_2/P_1V_1 = 2 \times 3 = 6 \\ S_2 - S_1 &= 6.9 \ln 6 - 1.986 \ln 2 \\ &= 10.99 \text{ Btu/mole} \end{aligned}$$

Values of $\int c_V\, dT/T$ and $\int c_P\, dT/T$, based on spectroscopic analysis and statistical mechanics, have been computed for various gases (Tables XXI and XXII, Appendix). These data eliminate the necessity of using the specific-heat relationships in the solution for entropy changes in problems dealing with gaseous mediums.

Values of $\int c_V\, dT/T$ may be used as the entropies for any volume line, and entropy values for other volume lines at the same temperatures may be determined by adding values of $R \ln (V_2/V_1)$ as indicated in Eq. (17). Likewise, values of $\int c_P\, dT/T$ may be used as the entropies for any pressure line, and entropy values for any other pressure line at the same temperatures may be determined by subtracting values of $R \ln (P_2/P_1)$ as indicated in Eq. (24). Obviously, if either table of values is used for a given line on a given diagram, the entropies of all other lines on the same diagram must be properly related to those of the given line by means of the Equation of State and Eqs. (17) and (24).

Example.—Assume that the initial temperature of the air in the two preceding examples is 520°R. Determine the entropy change for the process.

From the Equation of State,

$$T_2 = T_1P_2V_2/P_1V_1 = 520 \times 2 \times 3 = 3120°\text{R}$$

From Table XXI,

$$\int_{520}^{3120} c_V \frac{dT}{T} = 9.98 - 0 = 9.98$$

$$R \ln (V_2/V_1) = 1.986 \ln 3 = 2.18$$

Then, from Eq. (17), $S_2 - S_1 = 9.98 + 2.18 = 12.16$ Btu/°R

This result indicates the error in the two preceding examples because of the assumption of constant specific heat.

Properties Based on Deviation from Perfect Gas.—The perfect-gas Equation of State applies only for the condition when the pressure approaches zero. However, it has been shown that this equation may be used with fairly high accuracy whenever H or U is nearly a function of the temperature only. Otherwise, correction factors indicating the deviation from the perfect-gas condition provide a comparatively simple means for evaluating the various properties. The deviation of a medium from the perfect-gas condition is indicated by its *compressibility,** Z, which is determined from experimental data substituted in the relation

$$PV = ZRT \tag{1}$$

This deviation is indicated also by the *residual volume,** v, which is the difference between the volume computed from the perfect-gas equation and the actual volume. Thus,

$$v = RT/P - V \tag{2}$$

which combined with Eq. (1), results in

$$v = (1 - Z)RT/P \tag{3}$$

Multiplying by dP,

$$v\,dP = RT(dP/P - Z\,dP/P) \tag{4}$$

The term $Z\,dP/P$ may be replaced by df/f, f being a *pseudo pressure,* termed *fugacity,* which also indicates the deviation of a medium from the perfect-gas condition. At this condition Eq. (4) indicates that dP/P is equal to df/f since the residual volume is then zero. Thus, as P approaches 0, v approaches 0, and f approaches P. Integrating Eq. (4), after the foregoing substitution, results in

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* Data for various mediums will be found in *Industrial and Engineering Chemistry.* See Table XXIII, Appendix, for compressibility of methane, carbon dioxide, and mixtures of these gases. See Chart E for residual volumes of methane.

$$RT \ln (P/f) = \int_0^P v \, dP \tag{5}$$

since at the lower limit P/f approaches 1.

The ratio of f/P is known as the *activity coefficient.*

Example.—Determine the specific volume, compressibility, and the fugacity for CH_4 at 3,000 lb/in.² pr and 70 F.

From Chart E, Appendix, at the foregoing condition,

$$v = 0.0216 \text{ ft}^3/\text{lb}$$

$$V = RT/P - v = (1{,}545 \times 530)/(16 \times 3{,}000 \times 144) - 0.0216 = 0.0969 \text{ ft}^3/\text{lb}$$

in which the approximate molecular weight of methane (16) is used.

Also, $Z = PV/RT = (3{,}000 \times 144 \times 0.0969 \times 16)/1{,}545 \times 530 = 0.818$

A plot of v vs. P (Chart E) from 0 to 3,000 lb/in.² pr indicates a mean value of v of 0.0363 ft³/lb. Then,

$$\ln (P/f) = \frac{1}{RT}\int_0^{3{,}000} v \, dP = 0.0363 \times 16 \times 3{,}000 \times 144/(1{,}545 \times 530)$$

$$= 0.3064$$

$$P/f = 1.359 \qquad \text{and} \qquad f = 2{,}210 \text{ lb/in.}^2$$

The evaluation of H and S for mediums at high pressure by means of the compressibility factors or the residual volumes is illustrated in the Appendix.

Reduced Coordinates.—The *Law of Corresponding States* is that gases at the same *reduced* coordinates have approximately the same properties. The reduced coordinate is the ratio of the actual coordinate to the critical value for that coordinate. Thus,

$$T_r = T/T_c, \qquad P_r = P/P_c \qquad \text{and} \qquad V_r = V/V_c$$

where subscripts r and c indicate reduced and critical values, respectively. Usually P_r and T_r are used, since only two of the three elementary coordinates are required to define the state.

A plot of the compressibility, Z, vs. P_r at various values for T_r (Charts F and G, Appendix) may be used to evaluate volume values, from which the various properties may be determined as in the foregoing section.

Example.—Determine the specific and residual volumes for CH_4 at 3,000 lb/in.² and 70 F.

From Table IV, Appendix, the critical temperature and pressure are 343°R and 673 lb/in.², respectively. Then,

$$T_r = (460 + 70)/343 = 1.54 \qquad \text{and} \qquad P_r = 3{,}000/673 = 4.46$$

From Chart F, Appendix, for these conditions, $Z = 0.85$. Then,

$$V = ZRT/P = 0.85 \times 1{,}545 \times 530/(144 \times 3{,}000) = 1.61 \text{ ft}^3/\text{mole} = 0.100 \text{ ft}^3/\text{lb}$$

This compares with a value of 0.097 ft³/lb obtained in the foregoing example.

$$v = RT/P - V = 1{,}545 \times 530/(16 \times 144 \times 3{,}000) - 0.100 = 0.018 \text{ ft}^3/\text{lb}$$

This compares with a residual volume value of 0.0216 indicated on Chart E, Appendix, for this condition.

Obviously, such data for the given gas as illustrated on Chart E, Appendix, should be used, if available, rather than that obtained from the reduced-coordinate Chart F, Appendix.

Tables of Properties of Mediums.—Tables of properties of compressed liquid, saturated liquid and vapor, and superheated vapor (see Appendix) contain values of P, V, T, U, H, and S. The energy and entropy values are not absolute values but are above or below an arbitrary condition at which H and S are taken as zero. The difference between any two values of U, H, or S is an absolute change in U, H, or S, respectively, since the difference eliminates the datum condition.

Tables of properties for mediums in the gaseous state are usually given for a pressure of 1 atm* and contain values of T, U, H, and S. In many cases the medium is assumed to be a perfect gas, and table values of U and H are used for various pressures. However, a pressure correction of $R \ln (P_2/P_1)$ is always required for S values.† Where the deviation from perfect-gas conditions is appreciable, the corrections outlined in the foregoing section should be made.

Tables of superheated and gaseous mediums overlap in some cases. The superheated rather than the gaseous data should ordinarily be used in such cases. Some processes originate in the superheated (or solid, liquid, or vapor) region and end in the gaseous region, or vice versa. Obviously, in such cases the initial U, H, and S values for the superheated condition should not be subtracted from the end values, respectively, for the gaseous condition since the data in the two tables are not on the same basis. Instead, the change in U, H, or S to the upper limit of the superheated region should be added to the change in U, H, or S in the gaseous region above the upper limit in the superheated data.

General Equations for Properties of Mediums.‡—There are relationships among the various properties, specific heats, and coordinates of any medium that are usually called the *General Equations of Thermodynamics.*

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* Values of U and H are practically the same at 0 and 1 atm pr.

† The practice followed in this text is to use the values of $\int c\, dT/T$ for any desired pressure and to correct from this base for any other pressure.

‡ See Appendix.

These equations result from the combination of various thermodynamic and mathematical relationships and are invaluable in formulating or checking the properties of any medium such as tabulated in the Appendix.

Certain experimental data are required to formulate the Equation of State between P, V, and T for the medium. Some differential of one coordinate with respect to another is required in each General Equation. This is obtained from the Equation of State and, when substituted, results in a relation for a desired property.

Mollier or H-S Diagram.—This diagram is useful not only for portraying the properties of a medium but also for facilitating the solution of constant H, S, P, T, and x processes. The pressure lines diverge with an increase in entropy, and this expands the region in the neighborhood of the saturated-vapor line compared to that near the saturated-liquid line. Thus, the Mollier diagram for H_2O (Chart A, Appendix) is very useful in solving problems in this region. An area on this diagram does not have any particular significance.

Example.—Determine the quality and enthalpy of H_2O at the end of a constant-S change from an initial condition of 250 lb/in.^{2} and 600 F to a final condition of 10 lb/in.^{2}

The intersection of the 600 F and the 250 lb/in.^{2} lines (Chart A, Appendix) locates point 1 at an entropy of $S = 1.650$. At this point $H_1 = 1318.3$ Btu.

The intersection of $S = 1.650$ and $P = 10$ lb/in.^{2} lines locates point 2 at a moisture content of 0.092 or a quality of $x = 0.908$ and a value of $H_2 = 1053.0$.

H-S or U-S diagrams are also used for the solution of problems in the gaseous region. These may be constructed for a mixture of mediums (Chart H, Appendix). Also $(H + C)$ vs. S or $(U + C)$ vs. S diagrams (Chart I, Appendix) are useful for problems dealing with products of reactions.

Pressure-enthalpy Diagram.—This diagram (Chart B, Appendix) is useful for the solution of problems dealing with mediums in the regions near the saturated-liquid and saturated-vapor lines.

Example.—Saturated-liquid ammonia at a temperature of 60 F undergoes a constant-H process to a pressure of 20 lb/in.^{2} Determine the final quality and volume.

The intersection of the 60 F line and the saturated-liquid line (Chart B, Appendix) indicates an H value of 110 Btu. The intersection of this H line and the 20-lb line occurs at an x value of about 0.144 and a volume value of 2 ft^3.

EXERCISES

1. Plot the saturated-solid, -liquid, and -vapor lines for H_2O on T-S coordinates.

2. On the foregoing diagram plot the following lines: (a) quality lines for 10 per cent intervals, (b) constant-pressure lines for 0.0505, 100, and 5,000 lb/in.^{2}, (c) constant-volume lines for 4.432 and 2000 ft³/lb, (*d*) constant internal-energy lines for 600 and 1115 Btu/lb, (*e*) constant-enthalpy line for 1180 Btu/lb.

3. The following exercises deal with the coordinates and properties of H_2O:

a. Given $P = 150$ lb/in.² abs and $V = 1.508$ ft³/lb, determine T, S, U, and H.

b. Given $P = 300$ lb/in.² abs and $V = 2.005$ ft³/lb, determine T, S, U, and H.

c. Given $T = 300$ F and $V = 5.26$ ft³/lb, determine P, S, U, and H.

d. Given $P = 400$ lb/in.² abs and $H = 1150$ Btu/lb, determine V, T, S, and U.

e. Given $P = 485$ lb/in.² gage and $S = 1.78$ Btu/(lb × °R), determine V, T, U, and H. Barometric pressure = 30.55 in. Hg.

f. Given P = 2,000 lb/in.² abs and $T = 200$ F, determine V, S, U, and H.

g. Given $T = 20$ F and $H = 0$ Btu/lb, determine P, V, S, and U.

h. Given $P = 0.70$ in. Hg abs and $T = 70$ F, determine V, S, U, and H.

4. Plot a skeleton H-S diagram for 1 lb of CO_2 ranging from the saturated solid to the superheated region, including several constant P lines.

5. Plot a skeleton log P-H diagram for 1 lb of H_2O, including several constant V, T, U, S, and x lines.

6. *a*. Given $P = 180$ lb/in.² abs and $T = 160$, determine V, S, U, and H for 1 lb of ammonia.

b. Given $T = 0$ F and $H = 600$ Btu/lb, determine P, V, S, and U for 1 lb of ammonia.

7. *a*. Given $T = -70$ F and $S = 1.20$ Btu/(lb × °R), determine P, V, U, and H for 1 lb of carbon dioxide.

b. Given $P = 200$ lb/in.² abs and $T = 60$ F, determine V, S, U, and H for 1 lb of carbon dioxide.

8. *a*. Given $P = 100$ lb/in.² abs and $V = 0.681$ ft³/lb, determine T, S, U, and H for 1 lb of mercury.

b. Given $T = 535.4$ F and $H = 140$ Btu/lb, determine P, V, S, and U for 1 lb of mercury.

9. Plot a skeleton T-S diagram for 1 lb of gaseous N_2 including constant-volume lines of 10, 100, and 1,000 ft³/lb, and constant pressure lines of 1, 5, and 10 atm. Use the data in Table XXI, Appendix, for any one of the lines.

10. Check the entropy values in Exercise 9 at two points, having different pressures and volumes, by making use of the specific-heat equation for N_2 in Table II.

11. Check the internal-energy and enthalpy values for N_2 in Table XIX at 500, 2000, and 5000°R by making use of the specific-heat equation for N_2 in Table II.

12. Determine the specific weight of N_2 at 32 F and 1 standard atm.

13. The pressure of CO_2 is increased from 10 to 20 lb/in.² abs while its temperature is increased from 120 to 640 F. Determine the change in U, H, V, and S per mole of CO_2.

14. The same as Exercise 13, but for N_2.

15. A rigid bomb having an internal volume of 25 ft³ is filled with a perfect gas at a temperature of 140 F and at a pressure of 200 lb/in.² abs. Determine the moles of gas in the given volume.

16. The gas in Exercise 15 undergoes a chemical change such that the number of moles is decreased 20 per cent while the temperature increases to 1540 F. Determine the final pressure in the bomb.

17. Determine the mean values for c_P and c_V (*a*) for the CO_2 in Exercise 13, (*b*) for the N_2 in Exercise 14.

18. In a certain process the volume is tripled while the pressure is halved. Determine the change in entropy, if T_1 is 60 F (*a*) for 5 moles of CO_2, (*b*) for 1 mole of N_2.

19. Determine the specific volume of H_2O at a pressure of 1 lb/in.^{2} and a temperature of 1000 F, assuming H_2O to be a perfect gas. Compare with data for superheated H_2O.

20. The same as Exercise 19 but for a pressure of 2,000 lb/in.^{2}

21. Determine the residual volume, compressibility, and fugacity for H_2O at 1,000 lb/in.^{2} pr and 600 F.

CHAPTER V

THERMODYNAMIC PROCESSES

Classification of Processes.—It has been shown in Chap. III that it is desirable for analysis purposes to classify processes as being either nonflow or flow processes; also that flow processes are of two general types: steady-flow and nonsteady-flow processes.

Nonflow processes may also be classified according to the coordinate or property that may be held constant during the process, *i.e.*, constant pressure, constant internal energy, constant entropy, etc. A process may consist of two or more of such special processes, the end of one being the beginning of another special process. Also, a process may not have any of the coordinates or properties held constant.

Analysis and Solution of Processes.—The general method of process analysis has been outlined in Chap. III, and the energy equations for various processes have been formulated. A similar procedure is followed in this chapter; in addition the individual energy terms for which data are available are evaluated. The Energy Equation for the medium undergoing the process may be solved for one unknown energy term. If two unknown energy terms occur, it is necessary to express one in terms of the other, *i.e.*, to establish a second relationship involving the two unknowns, in order to effect a solution of the Energy Equation for the process.

The coordinates and properties for the medium, except P, V, and T for the gaseous state, are obtained usually from tabulated data (Appendix) for the given medium at conditions existing at the beginning and the end of the process. For perfect gases, the Equation of State in one of the forms

$$PV = MRT \qquad \text{or} \qquad P_1V_1/T_1 = P_2V_2/T_2 = \text{etc.}$$

is used to evaluate the defining coordinates.

The usual correction for other than perfect-gas conditions should be applied if neglecting to do so introduces appreciable error. However, in most cases perfect-gas conditions are assumed in order to simplify the analysis.

Most of the illustrations and exercises deal with ideal or reversible processes,* in which cases the areas beneath the paths representing the process on the *P-V* and *T-S* diagrams are equivalent to the work and heat values, respectively. The few irreversible cases included indicate the effect of irreversibility on the entropy of the medium. In such cases, work and heat values cannot be evaluated from the *P-V* and *T-S* diagrams, and in adiabatic cases *S* must not be assumed to be constant for the irreversible process. However, the Energy Equation may be applied to all processes.

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* See Chap. VII.

Reaction processes are treated in Chaps. IX and X.

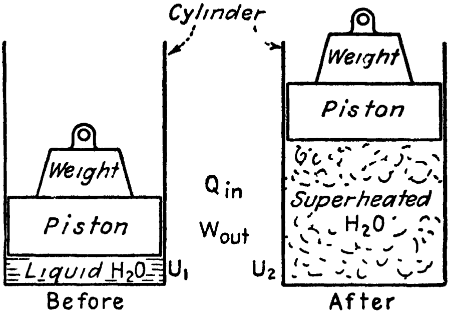

FIG. 30.—Sketch of apparatus for constant-pressure process.

NON-FLOW PROCESSES

Constant-pressure or Isobaric Process.—This process may take place in a cylinder with a vertical axis (Fig. 30), the medium being contained in the cylinder and held at the desired pressure by a weighted frictionless piston. If heat is added to the medium, the piston will rise and permit an increase in volume; if heat is abstracted, the piston will be lowered and the volume decreased.

The process may extend from the solid to the gaseous region, or vice versa. The path on the *T-S* diagram (Fig. 31) may consist of five connected parts: *AB*, *BC*, *CE*, *EF*, and *FG*. However, the path on the *P-V* diagram is a horizontal line. Starting at any point 1, and moving to the right on both diagrams to point 2, heat is transferred in since the entropy is increased, and work is done by the medium since the volume is increased. Thus, the Energy Equation for the process is

$$U_1 + Q_{in} = U_2 + W_{out} \tag{1}$$

Also,

$$W_{out} = \int_{V_1}^{V} P\,dV = P(V_2 - V_1) \tag{2}$$

Combining Eqs. (1) and (2) and adding the respective U and PV terms result in

$$H_1 + Q_{in} = H_2 \tag{3}$$

Thus, although no flow occurs into or out of the apparatus, and consequently there are no flow-work terms, the term enthalpy appears in the Energy Equation as a result of the foregoing manipulation.

Example.—H_2O is heated at a constant pressure of 200 lb/in.² from 0 to 1000 F Determine the heat transfer, the work, and the internal-energy change per pound of medium.

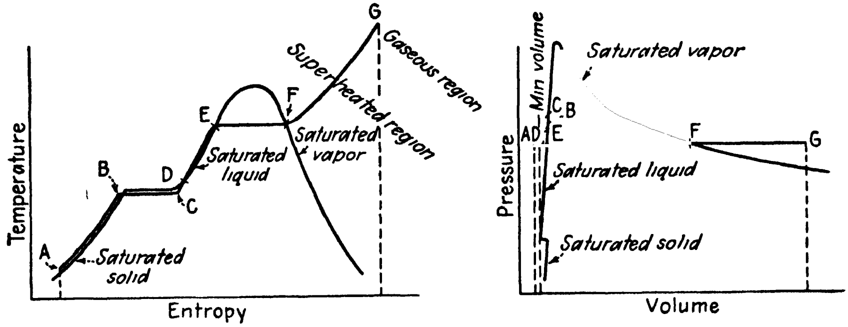

FIG. 31.—T-S and P-V diagrams for constant-pressure process for H_2O. (Not to scale.)

Inspection of Tables VI and VIII indicates that the medium is solid at the beginning and superheated vapor at the end of the process. The starting point is very nearly on the saturated-solid line. Since no other data are available, data for the saturated-solid are used.

Thus,
$$U_2 - U_1 = 1368.4 - (-158.9) = 1527.3 \text{ Btu}$$
$$W_{out} = P(V_2 - V_1) = 200 \times 144(4.309 - 0.017) = 123{,}610 \text{ ft-lb}$$
$$= 158.8 \text{ Btu}$$

Finally, from the Energy Equation for the process,

$$U_1 + Q_{in} = U_2 + W_{out}$$
$$Q_{in} = U_2 - U_1 + W_{out}$$
$$= 1527.3 + 158.8 = 1686.1 \text{ Btu}$$

The Q_{in} value may be checked by Eq. (3),

$$Q_{in} = H_2 - H_1$$
$$= 1528.0 - (-158.9) = 1686.9 \text{ Btu}$$

The Equation of State for the medium, if in the gaseous region, is

$$P_1V_1/T_1 = P_2V_2/T_2 \tag{4}$$

or, since p is constant,
$$V_1/V_2 = T_1/T_2 \tag{5}$$

Example.—One pound of H_2O at 10 lb/in.^{2} pr abs and an entropy of 2.3598 Btu/°R is heated at constant pressure to 3000°R. Determine the heat transfer, the work, and the internal-energy change.

Inspection of Table VIII indicates that the initial temperature is 1600 F or 2060°R, and that the enthalpy (and internal energy) is practically constant in this region. Consequently, the entire process may be assumed to be in the perfect-gas region.

The initial volume (Table VIII) is 122.7 ft^3/lb. From Eq. (5)

$$\begin{aligned} V_2 &= V_1T_2/T_1 = 122.7 \times 3{,}000/2{,}060 \\ &= 178.7 \text{ ft}^3 \end{aligned}$$

Then,

$$\begin{aligned} W_{\text{out}} &= P(V_2 - V_1) = 10 \times 144(178.7 - 122.7) \\ &= 80{,}640 \text{ ft-lb} = 103.7 \text{ Btu} \end{aligned}$$

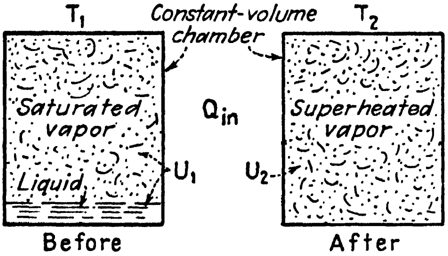

FIG. 32.—Sketch of apparatus for constant-volume process.

Substituting data from Table XIX in Eq. (3) results in

$$\begin{aligned} Q_{\text{in}} = H_2 - H_1 &= 25{,}118 - 14{,}910 = 10{,}208 \text{ Btu/mole} \\ &= 567 \text{ Btu/lb} \end{aligned}$$

Also from Table XIX,

$$\begin{aligned} U_2 - U_1 &= 19{,}160 - 10{,}818 = 8{,}342 \text{ Btu/mole} \\ &= 463 \text{ Btu/lb} \end{aligned}$$

The sum of $U_2 - U_1$ and W_{out} is 567 Btu, which checks the Q_{in} value.

Obviously, reversing the direction of the process so that the volume is decreased results in work in (instead of work out) and heat out (instead of heat in) in the Energy Equation for the process. Thus,

$$U_1 + W_{\text{in}} = U_2 + Q_{\text{out}} \tag{6}$$

Constant-volume or Isometric Process.—A constant-volume process that starts in either the solid or the liquid region usually ends in or very near one of these regions. However, a medium in the solid or liquid state may be heated at constant volume until its temperature is above the critical temperature, although the path of the process does not cross the saturated-vapor line. A process that starts in the mixture region may extend into the superheated or gaseous region (Fig. 33).

The container of the medium (Fig. 32) is assumed to undergo no change in volume, and consequently no work is done. Thus, the Energy Equation for a heating process is

$$U_1 + Q_{in} = U_2 \tag{1}$$

Example.—One pound of H_2O at a temperature of 200 F and a volume of 2 ft^3 is heated at constant volume to 1000 F. Determine the heat added.

Inspection of Table VI indicates that the starting point is in the saturated-mixture region since, at 200 F, 2 ft^3 is larger than V_f and smaller than V_g. Therefore, the initial pressure is 11.526 lb/in.^{2}

$$V_1 = V_f + xV_{fg} = 0.01663 + x33.62 = 2 \text{ ft}^3$$

or

$$x = 0.059$$

Then,

$$U_1 = U_f + xU_{fg} = 167.95 + 0.059 \times 906.1 = 221.4 \text{ Btu/lb}$$

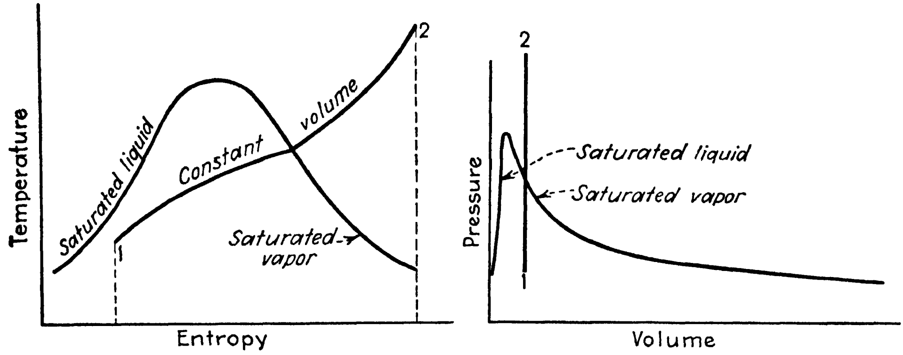

FIG. 33.—*T-S* and *P-V* diagrams for constant-volume process.

Inspection of Table VIII indicates that the final condition is between 400 and 500 lb/in.^{2} By interpolation at 1000 F, based on volume data

$$P_2 = 422 \text{ lb/in.}^2 \quad \text{and} \quad U_2 = 1363.9 \text{ Btu/lb}$$

and

$$Q_{in} = 1363.9 - 221.4 = 1142.5 \text{ Btu/lb}$$

The Equation of State indicates the following relation for this process in the perfect-gas region:

$$P_1/P_2 = T_1/T_2 \tag{2}$$

Example.—One mole of N_2 at 1000°R and a volume of 200 ft^3 is heated at constant volume to 3000°R. Determine the final pressure and the heat added.

The initial pressure is obtained from the Equation of State. Thus,

$$P = \frac{MRT}{V} = \frac{1 \times 1545 \times 1000}{200 \times 144} = 53.6 \text{ lb/in.}^2$$

Then from Eq. (2), $P_2 = P_1T_2/T_1 = 53.6 \times 3000/1000 = 160.8$ lb/in.^{2}

Substituting values from Table XIX into the Energy Equation for the process

$$Q_{in} = U_2 - U_1 = 14{,}236 - 2{,}416 = 11{,}820 \text{ Btu/mole}$$

Reversing the direction of the process results in Q_{out} instead of Q_{in}, and the Energy Equation becomes

$$Q_{out} = U_2 - U_1 \tag{3}$$

Constant-temperature or Isothermal Process.—This process may extend from the liquid or from the solid state to the gaseous state. If the process occurs at the melting point and the corresponding saturation pressure, both the solid and the liquid states may be involved.

This process might occur in a piston-cylinder mechanism (Fig. 34) which permits a sufficient increase in volume to maintain constant temperature as heat is added. The Energy Equation for the heating process is

$$U_1 + Q_{in} = U_2 + W_{out} \tag{1}$$

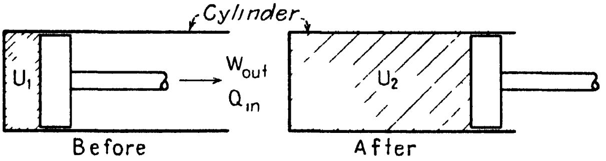

FIG. 34.—Sketch of apparatus for isothermal expansion process.

Since the process is represented by a horizontal line on the T-S diagram, the heat in can be determined from the relation

$$Q_{in} = \int_{S_1}^{S_2} T\,dS = T(S_2 - S_1) \tag{2}$$

and work out determined from the Energy Equation.

If heat transfer is out of the medium, $S_2 < S_1$ and

$$Q_{out} = -\,T(S_2 - S_1) \tag{3}$$

since all energy terms are positive in sign.

Example.—A pound of H_2O at 300 F and 1,000 lb/in.^{2} pr is heated at constant temperature (Fig. 35) until the volume increases to 8.773 ft^3. Determine the final condition and the work done.

An inspection of the 300 F column in Table VIII, Appendix, indicates

$$P_2 = 50 \text{ lb/in.}^2 \qquad S_2 = 1.6721, \qquad \text{and} \qquad U_2 = 1103.1 \text{ Btu/lb}$$

The saturation pressure for 300 F is 67.01 lb/in.^{2} (Table VI, Appendix).

The initial conditions obtained from Table V, Appendix, are

$$P_1 = 1{,}000 \text{ lb/in.}^2 \qquad S_1 = 0.43530$$

$$U_1 = 268.1 \text{ Btu} \qquad \text{and} \qquad V_1 = 0.01738 \text{ ft}^3\text{/lb}$$

Also, $Q_{in} = T(S_2 - S_1) = 760(1.6721 - 0.4353) = 940.0$ Btu

The work could be determined by planimetering the area under the path on the P-V diagram (Fig. 35) if drawn to scale. However, from Eq. (1),

$$\begin{aligned} W_{\text{out}} &= U_1 - U_2 + Q_{\text{in}} \qquad (4) \\ &= 268.1 - 1103.1 + 940.0 = 105.0 \text{ Btu} \end{aligned}$$

In the perfect-gas state the internal energy and enthalpy are functions of the temperature. Consequently, a constant-temperature process is also a constant-internal-energy and constant-enthalpy process. Thus, only work and heat-transfer items appear in the nonflow Energy Equations,

$$W_{\text{in}} = Q_{\text{out}} \qquad \text{or} \qquad W_{\text{out}} = Q_{\text{in}} \qquad (5)$$

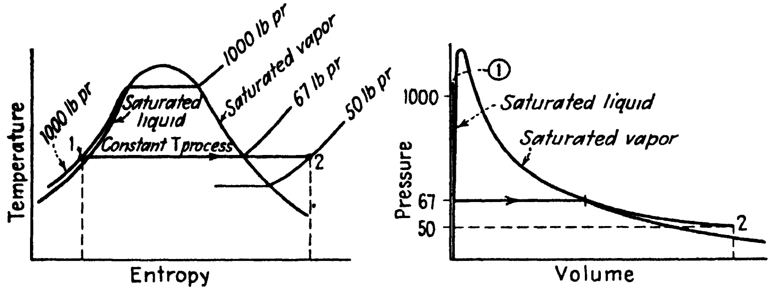

FIG. 35.—T-S and P-V diagrams for isothermal process.

The Equation of State indicates the following relationship for this process:

$$P_1V_1 = P_2V_2 = PV \qquad (6)$$

which is the expression for a hyperbolic curve on the P-V diagram.

The expression for work becomes

$$W = \int_{V_1}^{V_2} P\,dV = P_1V_1 \int_{V_1}^{V_2} \frac{dV}{V} = P_1V_1 \ln \frac{V_2{}^*}{V_1}$$

Example.—H_2O at 50 lb/in.^{2} pr and 1000 F expands isothermally to a pressure of 5 lb. Determine the final volume and the work done per pound of H_2O.

From Table VIII, Appendix,

$$V_1 = 17.352 \text{ ft}^3/\text{lb}$$

Assuming that the medium acts as a perfect gas,

$$V_2 = P_1V_1/P_2 = 17.352 \times 50/5 = 173.52 \text{ ft}^3/\text{lb}$$

and $W_{\text{out}} = P_1V_1 \ln (V_2/V_1) = 50 \times 144 \times 17.352 \ln (50/5) = 287{,}674$ ft-lb

This is equivalent to 369.8 Btu of heat added during the process.

From steam-table data, Table VIII, Appendix,

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[*] If V_2 is greater than V_1, the sign of the integral will be positive. Also the work is done by the medium. If V_2 is less than V_1, the sign of the integral will be negative. Hence, $W_{\text{in}} = -P_1V_1 \ln (V_2/V_1)$, since energy terms are always positive.

$$W_{out} = Q_{in} = T\,(S_2 - S_1) = 1460(2.2509 - 1.9964) = 371.6 \text{ Btu}$$

which is the correct solution for this problem.

Constant-entropy or Isentropic Process.—This process is represented by a vertical line on the T-S diagram (Fig. 36). Since $S_1 = S_2$, there is no area beneath the path on this diagram and consequently no heat transfer for the ideal or reversible process. The term *adiabatic* is applied to processes with no heat transfer.*

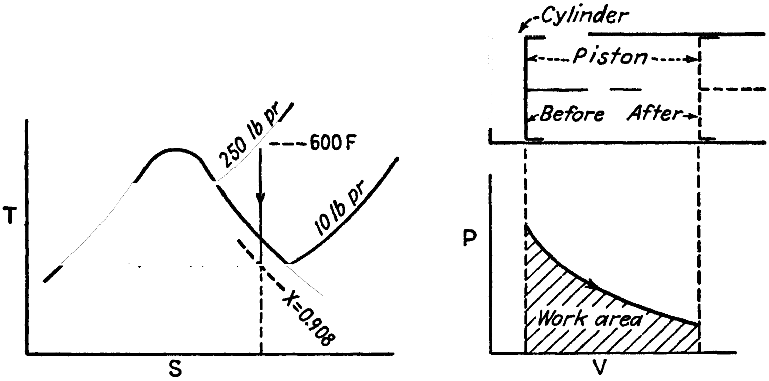

FIG. 36.—T-S, P-V, and apparatus diagram for the isentropic process.

If the volume is decreased during the process, the temperature increases and work is done on the medium. In this case the Energy Equation becomes

$$U_1 + W_{in} = U_2 \tag{1}$$

For the increasing volume process

$$U_1 = U_2 + W_{out} \tag{2}$$

Example.—H_2O at a pressure of 250 lb/in.^{2} and a temperature of 600 F expands isentropically to a pressure of 10 lb/in.^{2} Determine the final conditions and the work done per pound of medium.

The initial conditions are located in the superheated region (Fig. 36). Hence from Table VIII, Appendix,

$$U_1 = 1206.1 \text{ Btu/lb} \quad \text{and} \quad S_1 = 1.6495 \text{ Btu/(lb} \times {}^\circ\text{R)}$$

From Table VII, Appendix, the saturated vapor at a pressure of 10 lb/in.^{2} has an entropy of 1.7876.

Since,
$$S_1 = S_2 = 1.6495$$

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* Only reversible isentropic processes are adiabatic however, as will be shown in Chap. VII.

which is smaller than S_g at 10 lb pressure, it is obvious that the final condition is in the saturated-mixture region. Then,

$$S_2 = S_{x_2} = S_{g_2} - (1 - x_2)S_{fg_2}$$

or $$1 - x_2 = (1.7876 - 1.6495)/1.5041 = 0.092$$

Also, $$U_2 = U_{x_2} = U_{g_2} - (1 - x_2)U_{fg_2} = 1072.2 - 0.092 \times 911.1 = 988.4 \text{ Btu}$$

From Eq. (2), $$W_{\text{out}} = U_1 - U_2 = 1206.1 - 988.4 = 217.7 \text{ Btu}$$

In the perfect-gas region the internal-energy change can be obtained from Table XIX, Appendix, if the initial and final temperatures are known. However, if only one temperature and the pressure or volume change are known, the equation of the path must be known in terms of a pair of the coordinates in order to determine the temperature.

Equations (17) and (24), page 56, provide relations between V and T, and P and T, respectively, since the entropy is constant for this process. Thus,

$$\Delta S = \int_{T_1}^{T_2} c_V \frac{dT}{T} + R \ln \frac{V_2}{V_1} = 0 \qquad (3)^*$$

and

$$\Delta S = \int_{T_1}^{T_2} c_P \frac{dT}{T} - R \ln \frac{P_2}{P_1} = 0 \qquad (4)^*$$

Values for $c_V\, dT/T$ and $c_P\, dT/T$ may be obtained from Tables XXI and XXII, respectively, and may be used directly with Eqs. (3) and (4) in the solution of isentropic processes.

Example.—One mole of CO_2 is compressed adiabatically and isentropically in a piston-cylinder mechanism from 10 to 100 lb/in.^{2} abs pr. The initial temperature is 80 F. Determine the work required.

A sketch of the process (Fig. 37) indicates that the entropy is constant at 0.34, assuming the values in Table XXII apply to the 10-lb pr line in this case. The final temperature T_2 obviously is the same as T_2'. Hence, the entropy change from 2 to 2'. is equal to $R \ln (P_2/P_1)$, and

$$S_2' = S_1 + R \ln (P_2/P_1)$$
$$= 0.34 + 1.986 \ln 10 = 4.91$$

Since Table XXII was used for S_1, the value of S_2' of 4.91 at the same pressure indicates in the same table a value of 865°R for the temperature at 2' and 2.

Substituting internal-energy values for CO_2 from Table XIX into the Energy Equation for the process, Eq. (1), results in

$$139 + W_{\text{in}} = 2669$$

or $$W_{\text{in}} = 2530 \text{ Btu/mole}$$

The assumption of constant specific heat for small ranges of temperature near atmospheric is fairly accurate. With this assumption, the integration and manipulation of Eq. (3) result in

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* It should be noted that $R \ln (V_2/V_1)$ and $R \ln (P_2/P_1)$ are the entropy changes between two constant-volume and constant-pressure lines, respectively, at any temperature on the T-S diagram.

$$\left(\frac{T_2}{T_1}\right)\left(\frac{V_2}{V_1}\right)^{R/c_V} = \left(\frac{T_2}{T_1}\right)\left(\frac{V_2}{V_1}\right)^{k-1} = 1 \tag{5}$$

since $R = c_P - c_V$ and $c_P/c_V = k$ (6)

For perfect gases, $T_2/T_1 = P_2V_2/P_1V_1$ (7)

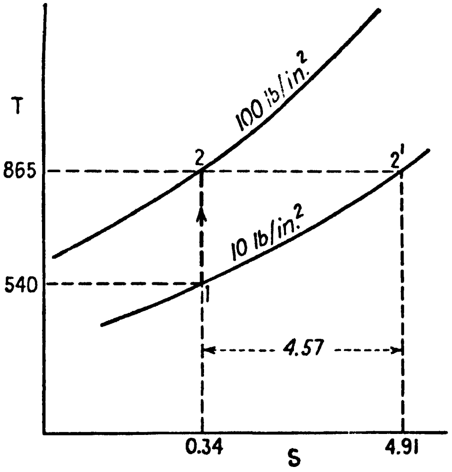

FIG. 37.—*T-S* diagram for solution of isentropic process with gases.

Combining Eqs. (5) and (7) results in

$$P_1V_1^k = P_2V_2^k \tag{8}$$

Also, from Eqs. (5) and (7),

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}} = \left(\frac{V_1}{V_2}\right)^{k-1} \tag{9}^*$$

* Equation (9) may be written

$$\ln P/P_0 = \frac{1}{R}\int_{T_0}^{T}\frac{c_P}{T}\,dT$$

since $(k-1)k = R/c_P$

If c_P is taken as a function of T only, the pressure ratio P/P_0 is a single function of the temperature if T_0 is made the datum temperature. This is also true for the volume ratio V/V_0.

With the foregoing as a basis a table of properties of dry air has been developed by Keenan and Kaye (*Trans.*, *A.S.M.E.*, 1943), assuming that air is a perfect gas. See also KEENAN, J. H., and J. KAYE, "Thermodynamic Properties of Air," John Wiley & Sons, Inc., New York, 1945.

The value of k is 5/3 for monatomic gases, the specific heats being constant for these gases. The value of k is very nearly 1.4 for the diatomic gases, for the temperature range of 0 to 400 F but decreases with temperature rise, since c_P and c_V for perfect gases have a constant difference regardless of temperature.

The work expression is determined by integrating the area beneath the *path on the P-V diagram. Thus,*

$$\text{Work} = \int_{V_1}^{V_2} P\,dV = P_1V_1{}^k\int_{V_1}^{V_2}\frac{dV}{V^k} = \frac{P_2V_2 - P_1V_1}{1-k} = \frac{R}{1-k}(T_2 - T_1) \qquad (10)$$

Example.—Solve the preceding example, assuming that $k = 1.4$ for CO_2.

From Eq. (9), $T_2 = 540 \times 10^{0.286} = 1043°\text{R}$
From Eq. (10), $W_{\text{in}} = 1.986\,(1043 - 540)/0.4 = 2497$ Btu/mole

These results indicate appreciable error, particularly in T_2, resulting from the use of $k = 1.4$. A value of k based on the actual specific heats at a mean temperature of about 800°R for this problem would result in a more accurate determination of the temperature and work. However, such data as in Tables XXI and XXII should always be used if available.

The terms c_V and c_P in Eqs. (3) and (4) may be replaced by their equivalent temperature functions (Table II, Appendix) and the resulting equations used for solving isentropic processes with gases when such data as that given in Tables XXI and XXII are not available.

Constant-internal-energy Process.—In this process, since

$$U_1 = U_2 \qquad (1)$$

the Energy Equation is

$$Q_{\text{in}} = W_{\text{out}} \qquad \text{or} \qquad W_{\text{in}} = Q_{\text{out}} \qquad (2)$$

depending on the direction of the process.

The work can be obtained from the area beneath the path plotted on the P-V diagram, or the heat transfer can be obtained from the area beneath the path when plotted on the T-S diagram (Fig. 38). The path followed in the saturated-mixture region makes accurate computation a difficult procedure. However, the area representing the heat transfer can be estimated quite accurately by dividing the area into strips of equal width (Fig. 38) or of equal temperature ranges as in the following example.

Example.—One pound of H_2O undergoes a constant-internal-energy process starting at 400 F and 247.31 lb/in.^{2} pr and extending to 200 F. Determine the work done during the process.

The data indicate that the process starts from the saturated-liquid line where $U = U_f = 374.12$ Btu. Then, dividing the process into equal temperature ranges,

T		U_f	U_{fg}	$U - U_f$	x	S_x	ΔS	T_{mean}	$T_{mean}\Delta S$
F	°R								
400	860	374.12	741.6	0	0	0.5664	0.0067	840	5.63
360	820	331.67	779.0	42.45	0.0545	0.5731	0.0093	800	7.44
320	780	289.99	813.7	84.13	0.1034	0.5824	0.0122	760	9.28
280	740	248.90	846.2	125.22	0.1480	0.5946	0.0157	720	11.30
240	700	208.26	876.8	165.86	0.1890	0.6103	0.0210	680	14.27
200	660	167.95	906.3	206.17	0.2275	0.6313			

$$\Sigma(T\ \Delta S) = Q_{in} = 47.92 \text{ Btu}$$

Thus,

$$Q_{in} = W_{out} = 47.92 \text{ Btu/lb}$$

In the perfect-gas region the constant-internal-energy process is a constant-temperature process which has already been treated.

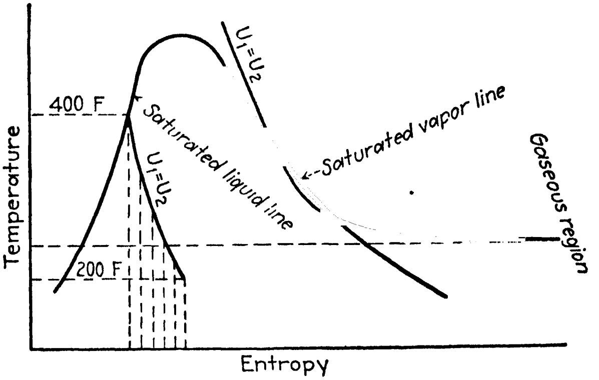

FIG. 38.—*T-S* diagram of constant-internal-energy process.

Constant-enthalpy Process.—In this process

$$H_1 = H_2 \tag{1}$$

The Energy Equation for the expansion process is

$$U_1 + Q_{in} = U_2 + W_{out} \tag{2}$$

and for the compression process is

$$U_1 + W_{in} = U_2 + Q_{out} \tag{3}$$

The methods used for evaluating both work and heat transfer are the same as in the case of the constant-internal-energy process.

In the perfect-gas region the constant-enthalpy process is a constant-temperature process which has already been treated.

Constant-quality Process.—This process occurs only in the saturated-mixture region, in which the quality x ranges from 0 to 1.00. For this process,

$$x_1 = x_2 \tag{1}$$

and the analysis is identical with that of the constant-internal-energy or -enthalpy process.

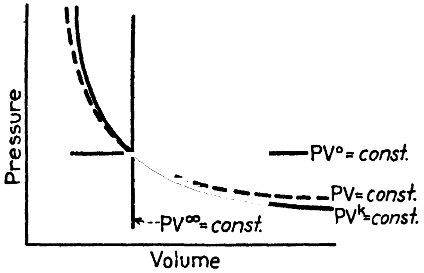

FIG. 39.—*P-V* diagram of various processes. (Gaseous region)

Polytropic Process.—The term *polytropic* is usually applied to any process that can be described by the equation

$$PV^n = \text{const} \tag{1}$$

The plotting of the process on *logarithmic P-V* coordinates results in a straight line and provides a means for the determination of the value of n from the slope of the line. Thus

$$\log P_1V_1^n = \log P_2V_2^n \tag{2}$$

from which

$$n = \frac{\log P_2 - \log P_1}{\log V_1 - \log V_2} \tag{3}$$

which is the slope of the line.

On rectangular coordinates (Fig. 39) the path of the isentropic process in the gaseous region (PV^k = const) has a greater slope than the isothermal process in the same region (PV = const). In the two quadrants in which these paths are located, the exponent of V ranges from 0 to ∞, while in the other two it ranges from 0 to $-\infty$.

The relations between the coordinates are the same as given by Eq. (9), page 73, with the substitution of n for k. Thus,

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} = \left(\frac{V_1}{V_2}\right)^{n-1} \tag{4}$$

The expression for work is the same as Eq. (10), page 74, with the substitution of n for k. Thus,

$$\text{Work} = \int_{V_1}^{V_2} P\,dV = \frac{P_2V_2 - P_1V_1}{1 - n} = \frac{R}{1 - n}(T_2 - T_1) \tag{5}$$

The heat transfer may be determined as usual from the Energy Equation.

The determination of the path or final conditions when the heat transfer, initial conditions, and final pressure or volume, but not temperature, are known, can be made by assuming various final temperatures and solving for corresponding values of n from Eq. (4). The correct values of T_2 and n will result in the correct value of the heat-transfer determination from the Energy Equation for the process.

Example.—One mole of carbon dioxide is compressed from 1 to 100 atm pr. The initial temperature is 40 F. The net heat transfer into the medium during the process is 5000 Btu/mole.

Assume T_2	1700°R	1800°R	1900°R
$l_{10}\,(T_2/T_1)$	0.5314	0.5563	0.5798
$(n-1)/n = 0.5\,l_{10}\,(T_2/T_1)$, Eq. (4)	0.2657	0.2782	0.2899
n	1.362	1.385	1.407
$W_{in} = -R\,(T_2 - T_1)/(1 - n)$, Btu/mole	6,585	6,710	6,820
$U_2 - U_1$, Table XIX, Appendix, Btu/mole	11,035	12,132	13,244
$Q_{in} = U_2 - U_1 - W_{in}$, Btu/mole	4,450	5,422	6,424

Interpolating for $Q_{in} = 5000$ Btu/mole results in values of

$$T_2 = 1755°\text{R} \qquad n = 1.375 \qquad \text{and} \qquad W_{in} = 6660 \text{ Btu/mole}$$

The value of n is appreciably higher than values of k at either 500 or 1755°R.

STEADY-FLOW PROCESSES

Engine or Turbine Process.—The medium used in a multicylinder engine or turbine flows steadily to and from the apparatus. In the ideal case with no heat transfer, the entropy of the medium is constant for the process. Usually, the initial conditions of the medium and the exhaust pressure are known. These data make possible the evaluation of the work that may be obtained from the process.

Example.—One pound of H_2O at a pressure of 200 lb/in.^{2} abs and a temperature of 700 F flows per second to a steam turbine. The exhaust pressure is 2 in. Hg abs. Determine the ideal horsepower of the turbine, assuming no heat transfer.

The Energy Equation for the process is

$$H_1 = H_2 + W_{out}$$

From Table VIII, Appendix, at 200 lb/in.² and 700 F, $H_1 = 1373.6$ Btu/lb and $S_1 = 1.7232$ Btu/(lb × °R).

From Chart A, Appendix, at $P = 2$ in. Hg and $S = 1.7232$, $H_2 = 961.8$ Btu, and $x = 0.861$.

Then,

$$\begin{aligned} W_{\text{out}} &= 1373.6 - 961.8 = 411.8 \text{ Btu/sec} \\ \text{Hp} &= 411.8 \text{ Btu/sec} \times 60 \text{ sec/min} \div 42.4 \text{ Btu/(min} \times \text{hp)} \\ &= 583 \text{ hp} \end{aligned}$$

Compressor Process.—The medium flows steadily to and from the multicylinder compressor or centrifugal fan or compressor (Fig. 22). In the ideal case with no heat transfer, the entropy of the medium is constant for this process. Usually, the initial conditions of the medium and the discharge pressure are known. These data make possible the evaluation of the work that is required for the process.

Example.—An aircraft engine has a displacement of 2,800 in.³ It operates at 1,800 rpm. It is desired to supply 1,400 in.³ of air at a pressure of 14.7 lb/in.² to the engine per revolution. The engine is in a plane at an altitude of 30,000 ft. Determine the horsepower required for an ideal adiabatic compressor or supercharger.

From Table III, Appendix, the initial air condition is 4.36 lb/in.² and −47.9 F. At this condition and at the final temperature for this process (which is assumed to be near normal atmospheric temperature at sea level) the specific heat for air is very nearly 0.24 Btu/lb per deg F diff., and $k = 1.4$ for the isentropic process.

Then, from Eq. (9), page 73,

$$T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}} = 412 \left(\frac{14.7}{4.36}\right)^{0.286} = 583°\text{R}$$

$$M = P_2V_2/RT_2 = 14.7 \times 144 \times 1{,}400 \times 30/(1{,}728 \times 1{,}545 \times 583)$$
$$0.0571 \text{ mole of air/sec}$$

The Energy Equation for the process is

$$H_1 + W_{\text{in}} = H_2$$

Thus,

$$\begin{aligned} W_{\text{in}} &= H_2 - H_1 = Mc_p(T_2 - T_1) \\ &= 0.0571 \times 28.95 \times 0.24(583 - 412) = 67.8 \text{ Btu/sec} \\ \text{Hp} &= 67.8 \times 60 \div 42.4 = 96.0 \end{aligned}$$

Practically the same results would be obtained by using the internal-energy and $\int c_p dT/T$ tables in the Appendix for the solution of this problem.

Effect of Heat Transfer on Engine and Compressor Processes.—The medium in the engine process is usually above atmospheric temperature throughout the entire process. Consequently, heat transfer is out of the medium. Heat transfer will occur from the medium in flowing from station 1 (Fig. 21) to the apparatus, and while flowing from the apparatus to station 2. In the ideal case no pressure drop is assumed in these sections. Hence, the heat transfer occurs at constant pressure for these sections (Fig. 40). Thus,

$$ {}_1Q_{1a} = H_1 - H_{1a} \tag{1} $$

may be used to evaluate H_{1a}, and a similar equation for the evaluation of H_2. Then, the Energy Equation for the process is

$$ H_1 = H_2 + \Sigma Q_{\text{out}} + W_{\text{out}} \tag{2} $$

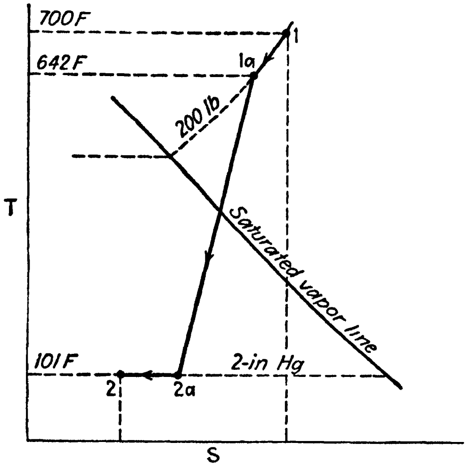

FIG. 40 —T-S diagram for engine process with heat transfer.

The heat transfer that occurs while the medium is in the apparatus undergoing the expansion process is indicated by the change in S and the path of the expansion process if frictionless.

Example.—Assume that 30 Btu of heat are transferred out of the medium from 1 to 1a (Fig. 40), 50 Btu from 1a to 2a, and 10 Btu from 2a to 2, the expansion process being a straight line on the T-S diagram. Initial conditions are 200 lb/in.^{2} and 700 F, and final pressure is 2 in. Hg. Determine the horsepower per pound of H_2O per second.

From Table VIII, Appendix, $H_1 = 1373.6$ Btu/lb and $S_1 = 1.7232$ Btu/(lb × °R).

Then $H_{1a} = 1373.6 - 30 = 1343.6$ Btu

From Table VIII, Appendix, $T_{1a} = 642$ F $= 1102$°R (see Fig. 40)

Point 2a is in the saturated mixture region at 2 in. Hg. Therefore $T_{2a} = 101 + 460 = 561$°R.

Then, $S_{2a} = S_{1a} - {}_{1a}Q_{2a}/T_{\text{mean}} = 1.7232 - 50 \times 2/(1102 + 561)$
$= 1.6631$ Btu/(lb × °R)

From Chart A, Appendix, at $S_{2a} = 1.6631$, $H_{2a} = 928.5$ Btu.

Then, $H_2 = H_{2a} - 10 = 918.5$ Btu
From Eq. (2), $W_{\text{out}} = 1373.6 - 918.5 - (30 + 50 + 10) = 365.1$ Btu
$\text{Hp} = 365.1 \times 60/42.4 = 516.7$

This compares with 583 hp for the ideal adiabatic process (p. 78). It should be noted that ${}_1Q_{1a}$ and ${}_{1a}Q_{2a}$ decrease the work obtained while ${}_{2a}Q_2$ does not.

The usual air compressor at sea level inducts air at atmospheric conditions and increases the temperature of the air being compressed. Thus, heat transfer is out of the medium in all parts of the process, except that of induction. During induction the air usually receives heat from the compressor and adjacent pipes which are at a higher temperature than the atmosphere (Fig. 41). At high altitudes heat may flow from the ducts and supercharger into the air during most of the process. However, each case must be examined to determine the direction of heat flow which may be in for one part and out for another part of the process. For the case illustrated in Fig. 41, the Energy Equation is

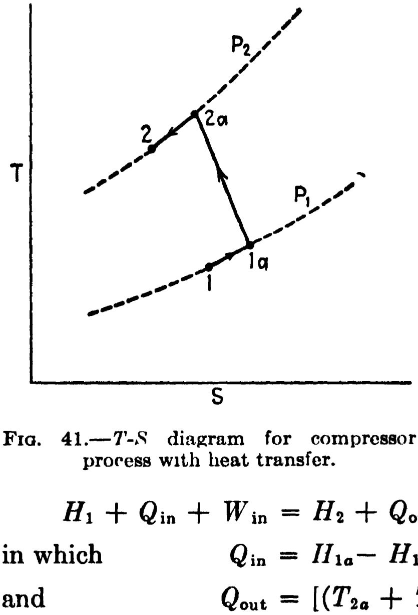

FIG. 41.—T-S diagram for compressor process with heat transfer.

$$H_1 + Q_{\text{in}} + W_{\text{in}} = H_2 + Q_{\text{out}} \tag{2}$$

in which
$$Q_{\text{in}} = H_{1a} - H_1 \tag{3}$$

and
$$Q_{\text{out}} = [(T_{2a} + T_{1a})/2]\,(S_{1a} - S_{2a}) + (H_{2a} - H_2) \tag{4}$$

assuming a straight-line process from $1a$ to $2a$.

Example.—Air at 60 F and 1 atm is compressed to 5 atm. Before actual compression the air temperature rises 10 F because of heat transfer from the intake pipe, ducts, valves, piston, and cylinder. During actual compression 150 Btu/mole of air are transferred out of the medium to the cylinder walls. During discharge 105 Btu/mole of air are transferred out of the medium. Determine the final temperature and work required for the entire process.

At 60 F, Table XIX, $H_1 = 1033$ Btu/mole of air
Referring to Fig. 41, $H_{1a} = 1033 + 7 \times 10 = 1103$ Btu

in which 7 is the approximate specific heat, Btu/mole, and 10 is the temperature rise.

Point $2a$ is determined by assuming various values for T_{2a} and evaluating entropy, S_{2a}, and heat transfer for the actual compression. Equation (24), page 56, is used, values for $\int c_p dT/T$ being given in Table XXII. Also, a straight-line compression process on the T-S diagram is assumed.

Assume T_{2a}	700°R	800°R	900°R
$\int c_p dT/T$ at P_1, Table XXII	2.09	3.02	3.86
$-\int c_p dT/T$ at P_1 and 530°R	−0.13	−0.13	−0.13
$-R \ln 5$	−3.20	−3.20	−3.20
$\Delta S = S_{2a} - S_{1a}$	−1.24	−0.31	0.53
T_{mean}, °R	615	665	715
$Q_{\text{out}} = -T_{\text{mean}} \Delta S$, Btu	762	206	−379

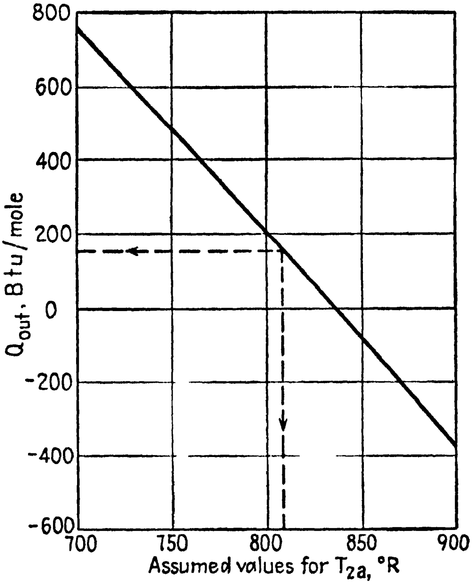

FIG. 42.—Plot of Q_{out} vs. T_{2a}.

Plotting heat transfer against T_{2a} (Fig. 42) and interpolating for a value of 150 Btu indicate 808°R for T_{2a}.

From Table XIX, H_{2a} at 808°R is 3049 Btu/mole

Then, $H_2 = H_{2a} - 105 = 3049 - 105 = 2944$ Btu

Interpolation in Table XIX indicates T_2 is 793°R for $H_2 = 2944$ Btu

Then,
$$\begin{aligned} W_{\text{in}} &= H_2 - H_1 + Q_{\text{out}} - Q_{\text{in}} \\ &= 2944 - 1033 + (150 + 105 - 70) = 2096 \text{ Btu} \end{aligned}$$

Throttling Process.—The throttling process is one of restricting flow and causing appreciable pressure drop through the throttling device which may be an orifice, nozzle, or partly closed valve in the line of flow. The pressure drop results in an increase in kinetic energy of the fluid stream as it leaves the restricting device. However, stations for analysis are located appreciably away from the restriction, particularly on the downstream side (Fig. 43), so that the fluid stream has the lowest possible kinetic energy. Usually, there is very little difference in kinetic energies between the points of analysis, so that, if no heat transfer occurs, the Energy Equation for the process is practically

$$H_1 = H_2 \tag{1}$$

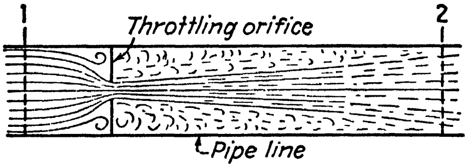

FIG. 43.—Diagram of throttling apparatus.

This does not mean that the process is one of constant H, for, between the stations for analysis, H decreases as the velocity increases (Fig. 44) and then increases to practically the original H as the velocity is decreased.

Example.—H_2O at 200 lb/in.^{2} pr and a quality of 0.97 flows into a throttling calorimeter which has a back pressure of 14.7 lb/in.^{2} Assuming no heat transfer, determine the final condition of the H_2O and the entropy change during the process.

From Chart A, at 200 lb/in.^{2} pr and $x = 0.97$, $H_1 = 1173.0$ Btu, and $S_1 = 1.515$ Btu/°R.

Also at $H_2 = 1173.0$ Btu and $P_2 = 14.7$ lb/in.^{2}, the medium is superheated, T_2 is 259 F, and S_2 is 1.789 Btu/°R.

Then, $$S_2 - S_1 = 1.789 - 1.515 = 0.274 \text{ Btu/°R}$$

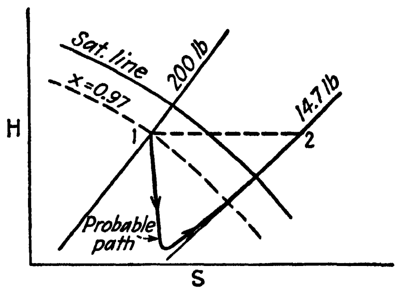

FIG. 44.—*H-S* diagram for throttling process.

The foregoing example indicates that the throttling process is not a so-called ideal or reversible process since entropy increases although no heat transfer occurs either to or from the medium. The dissipation by friction of some of the increase in kinetic energy occasioned by the pressure drop makes the throttling process irreversible. Thus, the flow could not be reversed in direction while maintaining the same condition of medium at each analysis station without the influence of outside energy effects (see Chap. VII).

Nozzle Process.—A medium usually approaches a nozzle at a moderate velocity, undergoes a pressure drop in the nozzle, and leaves at a higher velocity. In this case, station 2 for analysis (Fig. 45) is located at the exit of the nozzle where the velocity is a maximum, instead of downstream as for the throttling process.

The Energy Equation for the adiabatic process is

$$H_1 + KE_1 = H_2 + KE_2 \tag{1}$$

In the ideal case, frictionless flow may be assumed and then S_1 S_2 for the adiabatic process.

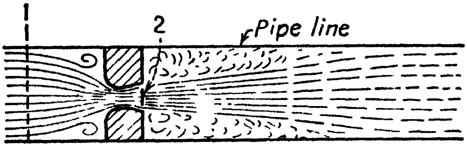

FIG. 45.—Diagram for nozzle flow.

Example.—H_2O at 200 lb/in.² and a quality of 0.97 has a velocity of 100 ft/sec as it approaches a nozzle. The pressure drops to 14.7 lb/in.² as the medium flows through the nozzle. Assuming adiabatic frictionless flow, determine the velocity of the H_2O leaving the nozzle.

From Chart A, Appendix, at 200 lb/in.² and $x = 0.97$, $H_1 = 1173.0$ Btu and $S_1 =$ 1.515 Btu/°R.

At $S_2 = S_1 = 1.515$ Btu/°R, and 14.7 lb/in.², $H_2 = 988.5$ Btu. Then, from Eq. (1),

$$KE_2 = 1173.0 + \overline{100}^2/(64.4 \times 778) - 988.5 = 184.7 \text{ Btu}$$

$$\text{Velocity} = \sqrt{64.4 \times 778 \times 184.7} = 3{,}040 \text{ ft/sec}$$

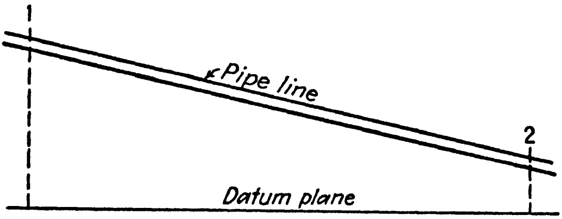

FIG. 46.—Diagram for pipe-line flow.

The frictionless nozzle process may be reversed, *i.e.*, the fluid may enter the nozzle exit at a high velocity and low pressure, and leave at a high pressure and low velocity at the original entrance. For such cases the device is termed a *diffuser*. Diffusers are used to convert the high kinetic energy of a medium into enthalpy with as much increase in pressure as possible.

Pipe-line Process.—All the usual energy terms except chemical energy and work are involved in the pipe-line process (Fig. 46). The Energy Equation is

$$PE_1 + KE_1 + H_1 = PE_2 + KE_2 + H_2 + Q_{out} \qquad (1)$$

This may be written

$$ht_1 + w_1^2/2g + U_1 + P_1/d_1 = ht_2 + w_2^2/2g + U_2 + P_2/d_2 + Q_{out} \qquad (2)$$

where w and d indicate velocity and specific weight, respectively.

The pressure drop along the line of flow tends to increase the fluid velocity, particularly for gases and vapors, while friction tends to decrease it.

Heat transfer from the fluid to the pipe and then to the surrounding atmosphere tends to prevent a temperature rise of the fluid because of the friction process. Assuming that the fluid enters the pipe line at atmospheric temperature, U_2 tends to equal U_1 and, if Q_{out} is small enough to be negligible, Eq. (2) may be written

$$ht_1 + w_1^2/2g + P_1/d_1 = ht_2 + w_2^2/2g + P_2/d_2 \qquad (3)$$

which is the *Bernoulli equation.* It is used extensively for analysis of liquid flow.*

Heat-transfer Processes.—When mediums flow steadily through heat-transfer apparatus, the *PE* and *KE* terms are usually eliminated since the difference of the entering and leaving terms for each form is usually negligible. Thus, the Energy Equation is

$$H_1 + Q_{in} = H_2 \qquad (1)$$

for the heating process or medium receiving heat,

and
$$H_1 = H_2 + Q_{out} \qquad (2)$$

for the cooling process or medium rejecting heat.

Example.—A surface condenser attached to the exhaust of a steam turbine has exhaust steam flowing into it at the rate of 1 lb/sec. The condition of the steam is 2 in. Hg pr and $x = 0.80$.

Cooling water at a temperature of 80 F is pumped into the condenser, flows through the condenser tubes, and leaves the condenser at a temperature of 90 F. The steam is condensed on the outer surface of the condenser tubes and leaves the condenser as a liquid at 90 F.

Determine the amount of cooling water required per pound of H_2O condensed.

The heat given up by the H_2O in being condensed and cooled to 90 F is equal to the heat received by the cooling water. Thus, neglecting *PE* and *KE* effects,

$$Q_{out} = (H_1 - H_2)_{hot} \qquad Q_{in} = M(H_2 - H_1)_{cold}$$

Combining both equations, since $Q_{in} = Q_{out}$ if no appreciable heat transfer occurs between the condenser and the atmosphere,

---

* See Chap. XI for further pipe-line flow analysis.

$$M = (H_1 - H_2)_{\text{hot}}/(H_2 - H_1)_{\text{cold}}$$
$$= (898.5 - 58.0)/(57.99 - 48.02) = 84.3 \text{ lb of cooling water}$$

The kinetic energy of the exhaust steam entering the condenser may be appreciable, and if so should be considered.

NONSTEADY-FLOW PROCESSES

Single-cylinder Engine or Compressor Processes.—The flow of medium into and out of the usual single-cylinder machine is intermittent and not steady flow. Steam is admitted to the single-acting engine cylinder (Fig. 47) during only a part of one stroke of the piston, and only during this time does flow to the engine occur. Likewise in the compressor, air flows into the cylinder during one stroke of the piston while it is compressed and discharged during the following stroke. These intermittent flows are the cause of appreciable pressure fluctuations in the lines leading to and away from machines of this type.

In the ideal case it is assumed that pressure fluctuations do not occur with intermittent flow. As a consequence, the flow work done on any given quantity of medium in being pushed past the stations for analysis is the same as for steady flow and the analysis of the ideal single-cylinder process is the same as for the multicylinder or turbine process. This can be shown by evaluating the work areas on the P-V diagrams for the compressor and complete-expansion engine processes.

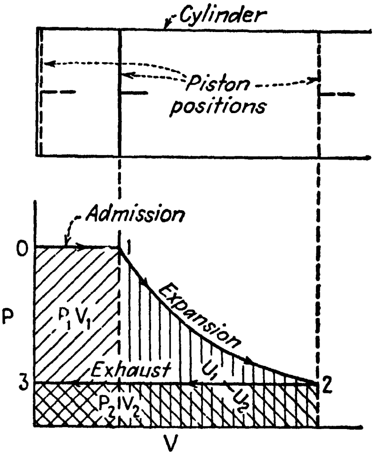

FIG. 47.—Steam-engine process with complete expansion.

Referring to Fig. 47, the work of admission from 0 to 1 is $P_1(V_1 - 0)$. The work of expansion, if adiabatic, has been shown to be equivalent to $U_1 - U_2$. The work of exhaust from 2 to 3 is $P_2(V_2 - 0)$ and is negative compared to the other work values. Hence, the work of the entire process is

$$W_{\text{out}} = P_1V_1 + (U_1 - U_2) - P_2V_2 = H_1 - H_2 \qquad (1)$$

Release Process.—The pressure of the medium in the engine cylinder at the end of expansion is usually higher than the pressure in the exhaust line. At the end of the expansion stroke the exhaust valve is opened and part of the medium is expelled because of pressure difference. In the limiting case the valve is assumed to open instantly and the piston to remain at the end of the stroke until the pressure in the cylinder is decreased to exhaust pressure.

The Energy Equation for the part remaining in the cylinder (Fig. 48) is

$$(M_B U_B)_1 = (M_B U_B)_2 + W_{B \text{ on } A} \qquad (1)$$

assuming ideal adiabatic expansion of part B in pushing part A out of the cylinder.

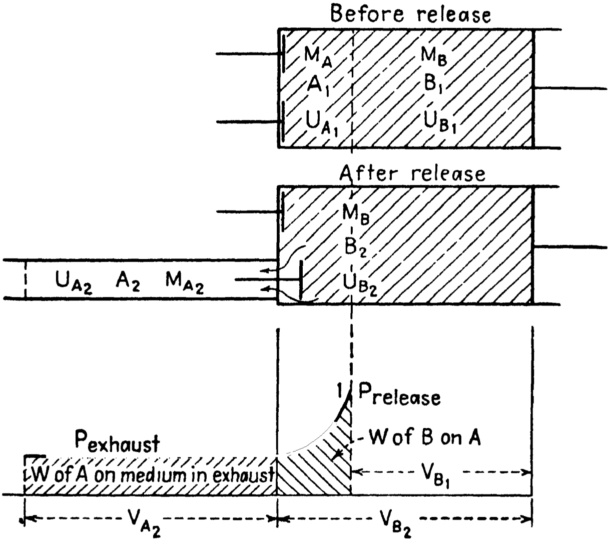

FIG. 48.—Diagram for release process.

The Energy Equation for the part escaping from the cylinder is

$$(M_A U_A)_1 + W_{B \text{ on } A} = (M_A U_A)_2 + W_{A \text{ on medium in exhaust}} \qquad (2)$$

This assumes that the kinetic-energy effects of part A because of pressure drop across the exhaust valve have been dissipated by friction and that all the kinetic-energy effects appear as energy associated with part A.*

Combining the two equations, noting that the work of A in pushing the exhaust medium along the exhaust line is $(M_A P_A V_A)_2$

$$MU_1 = (M_B U_B)_2 + (M_A U_A)_2 + (M_A P_A V_A)_2 = (M_B U_B)_2 + (M_A H_A)_2 \quad (3)$$

---

*If this analysis is applied to any small element of medium as it escapes from the cylinder, the work done on the escaping element approaches PV as a limit, in which V is the volume of the element before escape and P is the pressure in the cylinder at the instant of escape. Also, the flow work of each element on the medium already released is PV for the condition of the element after release. Hence, the enthalpy of each little element before escape is equal to its enthalpy after release. Thus, part A may be thought of as consisting of an infinite number of parts with enthalpy values ranging from the H of the medium at the beginning of release to the H of part B at the end of release.

Example.—The condition of the H_2O in a cylinder immediately before release is 50 lb/in.^{2} and a quality of 0.96. The pressure in the exhaust line is 14.7 lb/in.^{2} Determine the condition of the released part of the H_2O after release is completed.

The expansion of B is ideal and adiabatic (Fig. 49). From Chart A, Appendix, $S_1 = 1.609$ Btu/(lb × °R). At the same entropy and 14.7 lb/in.^{2}, $1 - x = 0.102$. Then, from Table VII,

$$\begin{aligned} U_1 &= U_g - (1 - x)U_{fg} = 1095.3 - 0.04 \times 845.4 = 1061.5 \text{ Btu} \\ U_{B_2} &= U_g - (1 - x)U_{fg} = 1077.5 - 0.102 \times 897.5 = 986.0 \text{ Btu} \\ V_1 &= V_g - (1 - x)V_{fg} = 8.515 - 0.04 \times 8.498 = 8.175 \text{ ft}^3 \\ V_{B_2} &= V_g - (1 - x)V_{fg} = 26.80 - 0.102 \times 26.78 = 24.07 \text{ ft}^3 \end{aligned}$$

Assuming 1 lb of medium in the cylinder before release,

$$M_B = V_1/V_{B_2} = 8.175/24.07 = 0.339 \text{ lb}$$

Substituting the foregoing values in Eq. (3) results in

$$1061.5 = 0.339 \times 986.0 + (1 - 0.339)H_{A_2}$$

or

$$H_{A_2} = 1100.1 \text{ Btu}$$

From Chart A, at 14.7 lb/in.^{2} and an H value of 1100.1 Btu, $S_{A_2} = 1.682$ Btu/ (lb × °R).

The released part has its entropy increased although the process is adiabatic. Hence, it is not an ideal or reversible process.

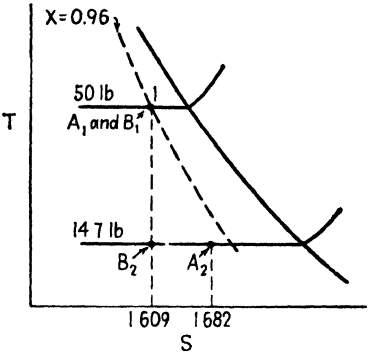

Fig. 49.—T-S diagram for release process.

Time Required for Release Process.—The pressure difference for the release process varies continuously from the value existing immediately before release to zero at the end of the process. Consequently, the rate of flow of the medium through the exhaust port varies throughout the process. Also, the quantity of medium released up to any instant in the process indicates the quantity of medium remaining in the cylinder at that instant. Thus, for any assumed pressure in the cylinder at any given time during the process, the instantaneous mass rate of flow can be determined and the integration of the area beneath the curve of mass-rate plotted against time must check the quantity released based on that remaining in the cylinder at the assumed pressure.

Example.—A 24- by 36-in. cylinder contains H_2O at 50 lb/in.^{2} and a quality of 0.96 immediately before release. The exhaust port area is 50 in.^{2} Determine the time required for release assuming an adiabatic process and full port opening during the process.

The Energy Equation for the evaluation of velocity of flow is

$$H_1 = H_2 + KE_2 \tag{1}$$

where subscript 1 refers to the instantaneous pressure condition in the cylinder at any instant during release, and subscript 2 refers to the condition in the exhaust pipe. Thus, the instantaneous velocity of escape is

$$w_2 = \sqrt{2g778(H_1 - H_2)} \tag{2}$$

No friction will be assumed in the port, and consequently H_1 and H_2 are at the same entropy. The mass rate of flow is the product of effective port area A_2 (which will be *assumed to be 0.65 of the actual area), the velocity w_2, and the density d_2.* A critical pressure ratio of 0.58 is used for the higher pressures (see Chap. XI).

Mass rate 0.65 w_2A_2/V_2
Cylinder volume 9.44 ft^3

Assume P_1, lb/in.^{2}	50	40	30	20	14.7
Critical P_2 or P_2, lb/in.^{2}	29	23	17	14.7	14.7
H_1 at S_1, Btu	1137.2	1120.7	1100.0	1071.8	1051.1
H_2 at S_1, Btu	1097.2	1080.9	1060.4	1051.1	1051.1
$H_1 - H_2$, Btu	40.0	39.8	39.6	20.7	0
w_2 ft/sec	1,414	1,411	1,407	1,020	0
V_2, ft^3/lb	13.12	16.2	21.2	24.1	24.1
Mass rate, lb/sec	24.4	19.7	15.0	9.6	0
V_1 at S_1, ft^3/lb	8.18	9.96	12.82	18.33	24.06
Mass in cyl, $9.44/V_1$, lb	1.153	0.948	0.736	0.515	0.392
Mass released, lb	0	0.205	0.417	0.638	0.761
Time × 10^2, sec	0	0.93	2.15	3.95	6.51

The mean rate of flow while the pressure in the cylinder is decreasing from 50 to 40 lb/in.^{2} is about 22 lb/sec. During this time period 0.205 lb is released. The time required will be approximately $0.205/22 = 0.0093$ sec. Plotting the mass rate of 19.7 lb/sec at this time (Fig. 50), etc., results in the approximate rate-of-flow vs. time curve. This indicates a time for release of about 0.065 sec at the point where the mass rate is zero.

If the mass-rate curve has very much curvature, the area under each part of it should be checked against the amount released, and the time value for the point should be shifted until this check is obtained.

In actual practice appreciable time is required to open the exhaust port. Also, the piston is moving toward outer dead center as the exhaust port is being opened. The variation of port opening and cylinder volume can be determined from the mechanics of valve- and piston-operating mechanism, respectively. The variation of cylinder volume affects only the mass of medium in the cylinder at any assumed pressure and can be accounted for readily as indicated in the foregoing example.

The variation in port area is plotted against time, and the area corresponding to estimated time is used to evaluate the mass rate for that time. Otherwise, the solution is made in the same manner as in the foregoing example.

Receiver-filling Processes.—The filling of a tank or receiver with air or other compressible fluids is a process in which conditions in the receiver are varying throughout the process. The filling may be accomplished by permitting the medium to flow from a tank under high pressure into the tank to be filled. The process may be either adiabatic or isothermal for the limiting cases. The analysis is similar to that of the release process, the entropy increasing during the process although no heat transfer occurs.

A common receiver-filling process, in which the volume of the receiver varies, occurs in each cycle of the reciprocating steam engine. All reciprocating steam engines have clearance volume (Fig. 51) into which part of the steam remaining in the cylinder during the last part of the exhaust stroke is compressed. At the end of compression the pressure is usually less than the pressure of the steam supplied to the engine. In the ideal case the admission valve opens at the end of compression and steam flows into the clearance space until supply pressure is attained in the cylinder.

The Energy Equation for this part of the process is

$$MH + M_{cl}U_1 = (M + M_{cl})U_2 \quad (1)$$

where M is the amount of steam admitted from 1 to 2, M_{cl} is the amount of steam initially in the clearance volume, and H is the enthalpy of the steam supplied.

The solution of this part of the process is based on the volume of $(M + M_{cl})$ lb of steam at supply pressure P_2 and internal energy U_2 This volume must equal the cylinder clearance volume.

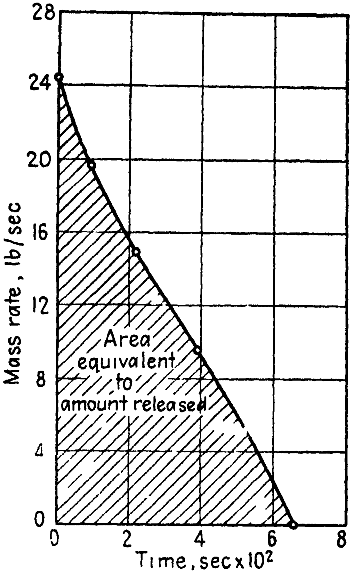

FIG 50—Mass rate vs time for release process

During the second part of the filling process, the piston moves and more steam flows into the engine maintaining the supply pressure in the cylinder until cut off.

The Energy Equation for this part of the process is

$$M'H + (M + M_{cl})U_2 = (M' + M + M_{cl})U_3 + W_{out} \quad (2)$$

where M' is the amount of steam admitted from 2 to 3. The solution for M' is similar to that of the first part of the process.

In the ideal case the expansion process after cutoff and the exhaust stroke including compression are assumed to be adiabatic and isentropic. The release process, 4 to 5, is irreversible but not for the part that remains in the cylinder in the ideal case (see Release Process, page 85). Thus, the specific entropy of the steam in the clearance volume at the beginning of the filling process must be the same as the specific entropy of the steam in the cylinder at the end of the filling process. Since the filling process results in an increase of entropy, the final entropy after filling is higher that that of the steam supplied.

The filling of a receiver with a compressor imposes variable discharge conditions on the compressor. Assuming an adiabatic process in which M moles of medium at initial conditions of P_1 and T_1 (Fig. 52) are to be pumped into a receiver which contains M_1 moles of the medium at its initial conditions of P_1' and T_1', the Energy Equation for the process is

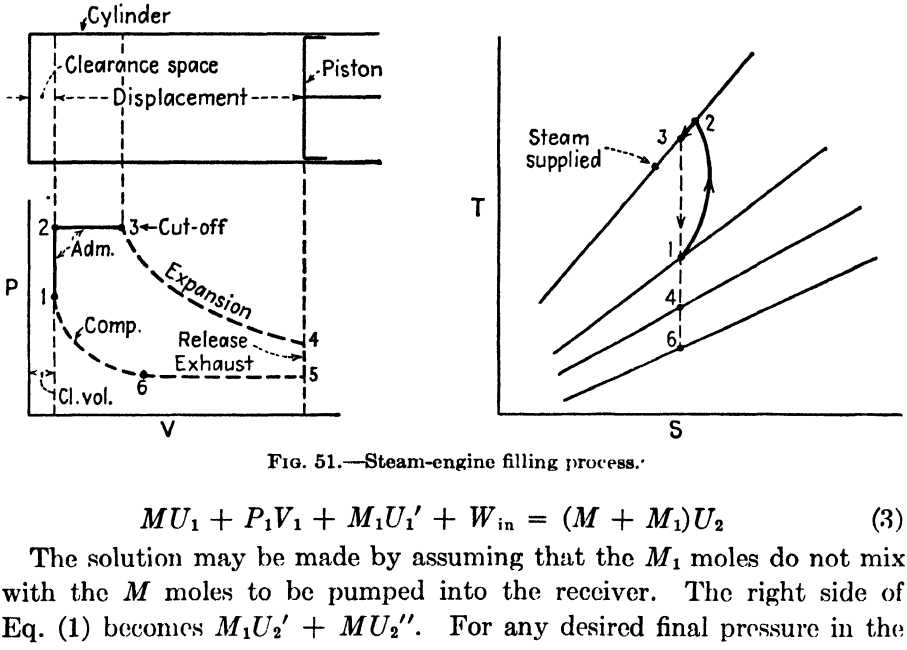

FIG. 51.—Steam-engine filling process.

$$MU_1 + P_1V_1 + M_1U_1' + W_{\text{in}} = (M + M_1)U_2 \qquad (3)$$

The solution may be made by assuming that the M_1 moles do not mix with the M moles to be pumped into the receiver. The right side of Eq. (1) becomes $M_1U_2' + MU_2''$. For any desired final pressure in the tank, the final temperatures of both parts in the tank can be determined either from the entropy equation or tables, or from the approximate relation

$$T_2 = T_1(P_2/P_1)^{\frac{k-1}{k}} \qquad (4)$$

if a perfect gas, or from the Mollier or other diagram of the medium involved.

The Equation of State or the properties of the medium may be used to determine the value of M. Thus, if a perfect gas,

$$P_2V_2 = (M_1 + M)RT_2 \qquad (5)$$

A common case is that of filling an air receiver that initially contains air at atmospheric conditions. The assumption of isothermal compression and cooling of the receiver to maintain the initial temperature eliminates the internal-energy terms from Eq. (3) and adds a heat-out term, resulting in

$$P_1V_1 + W_{\text{in}} = Q_{\text{out}} \tag{6}$$

The heat to be removed during the process will be the same as that required in isothermally compressing, in a single compression process, all of the medium involved. Thus, if the medium is a perfect gas,

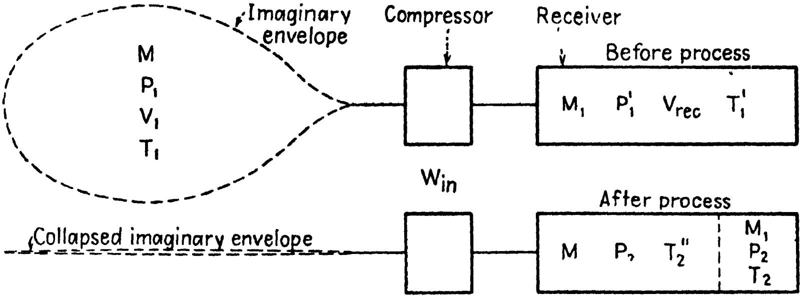

FIG. 52.—Sketch for adiabatic compressor-receiver filling process (The sketch for the isothermal process would have T_1 in the receiver before the process and $(M + M_1)$, P_2 and T_1 in the receiver after the process Also Q_{out} from both the compressor and the receiver would be indicated)

$$Q_{\text{out}} = T_1\,\Delta S = T_1(M + M_1)R \ln (P_2/P_1) \tag{7}$$

which substituted in Eq. (6) makes possible the solution for the work requirement.

The Energy Equation for the isothermal-compressor and adiabatic-receiver case* is

$$(M + M_1)U_1 + P_1V_1 + W_{\text{in}} = Q_{\text{out}} + (M + M_1)U_2 \tag{8}$$

in which case the initial conditions of the medium ahead of the compressor and in the receiver are the same.

Since $W_{\text{in}} = Q_{\text{out}}$ for the isothermal compressor, Eq. (8) becomes

$$(M + M_1)(U_2 - U_1) = P_1V_1 \tag{9}$$

Assuming constant specific heat and a perfect gas,

$$(M + M_1)c_v(T - T_1) = MRT_1 \tag{10}$$

or

$$T = T_1\left[1 + \frac{MR}{(M + M_1)c_v}\right] \tag{11}$$

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* This case and the analysis were suggested by the work of G. Zerkowitz, Second Law of Thermodynamics . . . with particular Reference to Steam Engines, *Trans. A.S.M.E.*, **66**, A-108 (1944).

where T is the final temperature when M moles of gas have been pumped into the receiver.

The work of isothermally compressing an increment dM of gas is equal to the heat transfer. Thus,

$$dW_{\text{in}} = T_1\, dS = T_1\, dMR \ln (P/P_1) \tag{12}$$

The relation between P and M is given by the Equation of State.

$$PV_{\text{rec}} = (M + M_1)RT \tag{13}$$

Combining Eqs. (11) and (13) results in

$$P = \frac{RT_1}{V_{\text{rec}}}\left(M + M_1 + \frac{MR}{c_V}\right) \tag{14}$$

or

$$dP = \frac{RT_1}{V_{\text{rec}}}\left(1 + \frac{R}{c_V}\right)dM \tag{15}$$

Combining Eqs. (12) and (15) and simplifying result in

$$dW_{\text{in}} = \frac{V_{\text{rec}}}{k} \ln \frac{P}{P_1}\, dP \tag{16}$$

or

$$W_{\text{in}} = \frac{V_{\text{rec}}}{k}\left(P_2 \ln \frac{P_2}{P_1} - P_2 + P_1\right) \tag{17}$$

The time required to pump M moles of medium into the receiver in any of the foregoing cases depends on the compressor displacement per unit of time and the effect of discharge pressure on volumetric efficiency (see Chap. VIII). Variation of supply conditions also would influence the time requirement.

EXERCISES

Nonflow Processes

1. One mole of air is cooled from 2000 to 60 F at a constant pressure of 1 atm. Determine the heat removed, the change in internal energy, and the work done in a nonflow process. *Ans.* $W_{\text{out}} = 3850$ Btu.

2. CO_2 is heated from −75 to 500 F at a constant pressure of 10 lb/in.^{2} Determine the heat added, the change in internal energy, and the work done in a nonflow process.

3. CO_2 is cooled from 150 F and 300 lb/in.^{2} to −100 F in a constant-volume process. Determine the heat removed when the maximum liquid is obtained, when the minimum solid and no liquid occur, and for the entire process. *Ans.* $Q_{\text{out}} = 233.9$ Btu.

4. One mole of air at 14.7 lb/in.^{2} and 60 F is heated to 2000 F in a constant-volume process. Determine the heat added and the final pressure.

5. CH_4 is heated from 60 F and 3,000 lb/in.^{2} to 2000°R in a constant-volume process. Determine the heat added and the final pressure, assuming a perfect-gas condition.

6. One pound of H_2O having a volume of 1 ft³ at 67.013 lb/in.² is heated at constant temperature in a nonflow process to a pressure of 30 lb/in.² Determine the heat added and the work done. *Ans.* $Q_{in} = 847$ Btu. $W_{out} = 136$ Btu.

7. Air is expanded at a constant temperature of 140 F from 10 to 2 atm in a piston-cylinder mechanism. Determine the heat added and the increase in entropy per pound of air. *Ans.* $\Delta S = 0.11$ Btu/°R.

8. CH_4 is compressed at a constant temperature of 140 F in a compressor from 1,000 to 5,000 lb/in.² Determine the heat removed and the decrease in entropy per mole of gas, assuming a perfect-gas condition.

9. A pound of CO_2 is compressed isentropically from a temperature of −80 F and a volume of 1 ft³ until a saturated liquid is obtained. Determine the final conditions and the work required. Check the work value by plotting the path on P-V coordinates and evaluating the work area.

10. Develop the equation in terms of T and V, and T and P, for the adiabatic isentropic change for a perfect gas using the specific heat equation for CO, Table II, Appendix.

11. Plot on logarithmic P-V coordinates and then transfer the pressure-volume data to rectangular P-V coordinates, the paths indicated by the equations PV = const, $PV^{1.4}$ = const, and PV^2 = const. All paths are to intersect at $P = 100$ lb/in.² abs and $V = 50$ ft³/mole of medium. Note that these paths are straight lines on the logarithmic coordinates so that only two points need be computed for each path.

12. One mole of CO is compressed adiabatically and isentropically from 1 to 100 atm. The initial temperature is 60 F. Determine the initial and final volumes and the work required using (*a*) the tables in the Appendix, (*b*) the equation developed in Exercise 10 for determining T_2, and the specific heat equation for determining the internal-energy change, (*c*) constant specific heats and the relations based on PV^k = const. *Ans.* (*a*) $W_{in} = 7019$ Btu/mole.

13. H_2O at 100 F and a volume of 160 ft³/lb is compressed to a pressure of 300 lb/in.² while a constant quality is maintained. Determine the heat transfer and work done per pound of H_2O. Evaluate the heat transfer by plotting the path of the process on a much expanded entropy scale, and evaluating the area beneath the path on a T-S diagram. *Ans.* Net $Q_{in} = 27.5$ Btu.

14. N_2 is expanded in a cylinder from 3000°R to ten times its initial volume. The heat transferred from the N_2 to the cylinder walls is one-fifth the decrease in internal energy. Determine the final conditions, the heat transferred and the work done per mole of medium (*a*) assuming the path is described by PV^n = const, and that $k = 1.4$, (*b*) using the Energy Equation and the entropy tables.

15. H_2O in a piston-cylinder mechanism has its condition changed from a pressure of 14.7 lb/in.² and a volume of 10 ft³ to a pressure of 50 lb/in.² and a temperature of 400 F in a process the path of which is a straight-line path on the T-S diagram. Determine the work done and the heat transfer. Check the work done by evaluating the area beneath the path on the P-V diagram. *Ans.* $W_{out} = 49.3$ Btu.

Steady-flow Processes

16. One pound of air at a pressure of 200 lb/in.² and 940 F flows per second to a turbine. The exhaust pressure is 14.7 lb/in.² abs. Determine the ideal horsepower of the turbine assuming no heat transfer. Compare the result with that obtained when using 1 lb of H_2O with the same conditions.

17. Saturated liquid ammonia at a temperature of 80 F flows to an expander. The pressure is reduced to 40 lb/in.^{2} in the machine and the ammonia is discharged at this pressure. Determine the final condition of the ammonia and the ideal work of the expander, assuming no heat transfer. *Ans.* $W_{out} = 5.2$ Btu/lb.

18. Determine the ideal horsepower required for a supercharger for the engine in the example on page 78 if the engine is at sea level with air at 60 F and the supercharger-pressure ratio is the same as in the example.

19. Assume that the supercharger in Exercise 18 is cooled sufficiently to have isothermal compression. Determine the work requirement and the heat removed. *Ans.* $W_{in} = 798$ Btu/mole.

20. Assume that the ammonia in Exercise 17 is throttled adiabatically to the final pressure of 40 lb/in.^{2} Determine the final condition and increase in entropy.

21. Assume that 30 Btu/lb of ammonia flow into the medium during the throttling process in Exercise 20. Determine the final conditions and the increase in entropy.

22. It is proposed to cool liquid H_2O at 80 F and atm pr by flowing it through spray nozzles into a flash chamber in which the pressure is maintained at 0.2 lb/in.^{2} abs by ejectors or vacuum pumps. To what temperature can the liquid be cooled if the process is adiabatic? Determine the ideal work, per pound of cooled liquid obtained, to maintain the given pressure.

23. The throttling orifice in Exercise 20 is located in a 3-in. pipe line and the flow rate is 2 lb/sec. Determine the correction for kinetic energy effects.

24. Air having a temperature of 140 F and a pressure of 14.7 lb/in.^{2} abs is flowing with a velocity of 1,000 ft/sec into a diffuser in which the velocity is reduced to 200 ft/sec. Assuming an ideal adiabatic process, determine the final condition of the air leaving the diffuser. *Ans.* $P_2 = 22.5$ lb/in.^{2}

25. The H_2O in the example on page 84 enters the condenser through an inlet nozzle having an area of 0.4 ft.^{2} Recompute the example including the kinetic energy effect.

Nonsteady-flow Processes

26. A hydrogen container has a volume of 2 ft.^{3} The pressure of the hydrogen is 500 lb/in.^{2} What size balloon can be filled at a pressure of 15 lb/in.^{2} at the conditions existing immediately after the H_2 is released? Initial temperature of the H_2 is 60 F. Assume that the process is adiabatic and use constant specific heats based on the temperature of 60 F. *Ans.* 46 ft^3.

27. A 10-ft^3 receiver is completely evacuated. A crack develops and air rushes into the receiver.

a. Determine the temperature of the air in the receiver if it fills very quickly.

b. Analyze the process if the receiver fills slowly.

28. Solve the process in Exercise 26 assuming that it takes place very slowly with all possible heat-transfer effects. The atmospheric temperature is 60 F.

29. Determine the net heat transferred to and from the container and the balloon in Exercise 28.

30. At the end of the compression process in an engine cylinder the H_2O is at a pressure of 150 lb/in.^{2} abs and has a quality of 0.98. Boiler steam at a pressure of 300 lb/in.^{2} abs and at a temperature of 500 F is permitted to flow into the clearance space until boiler pressure is attained in the cylinder.

a. Determine the weight ratio of the steam admitted to that compressed in the cylinder.

b. Determine the condition (T and S) of the H_2O in the cylinder at the end of the filling process.

31. A steam engine cylinder has a clearance volume of 5 per cent of the piston displacement. Compression of the steam remaining in the cylinder occurs when the piston has completed 70 per cent of the exhaust stroke. Steam is admitted while the piston is at the end of its stroke, during which time the supply pressure is attained in the cylinder. More steam is admitted for 25 per cent of the expansion stroke, maintaining supply pressure in the cylinder.

Solve for the condition of the steam at the end of each part of the filling process, assuming a supply condition of 300 lb/in.^{2} and 500 F. Assume that the steam at the beginning of the compression process is at a pressure of 14.7 lb/in.^{2}, and at an entropy of more than the supply condition. Assume adiabatic processes with isentropic compression and isentropic expansion after the second part of the process, and the entropy of the steam at the end of the second part of the admission process should equal that assumed for the beginning of compression.

32. Plot the path of the filling processes for the data in Exercise 31, by assuming several pressures for the first part of the admission process and computing the entropy.

33. Assume that the exhaust valve in the example on page 87 begins to open at 45 deg before bottom-center piston position and opens directly with time until wide-open at bottom center. The piston motion is represented by a simple harmonic. Determine the pressure of the medium in the cylinder at bottom center for an engine speed of 150 rpm.

34. Air is to be pumped into a 10-ft^3 receiver until a pressure of 150 lb/in.^{2} gage is attained. The tank initially contains air at atmospheric conditions of 14.7 lb/in.^{2} and 60 F. Determine the work required and the moles of air pumped into the receiver (*a*) for an adiabatic process, (*b*) for an isothermal process, (*c*) for an isothermal-compressor and adiabatic-receiver process.

Sketch P-V diagrams, with receiver and cylinder-displacement volumes adjacent to each other, showing the paths for several consecutive compressor cycles. Assume compressor displacement is about one-half of the receiver volume and compressor clearance is about 20 per cent of displacement.

35. The same as (*a*) in Exercise 34, except that the receiver is completely evacuated at the beginning of the process. A pressure-regulating device (throttling valve) is inserted in the pipe line between the compressor and the receiver and maintains a constant discharge pressure of 150 lb/in.^{2} for the compressor during the entire process.

36. H_2O at 14.7 lb/in.^{2} and with a specific volume of 25 ft^3/lb is to be pumped into a 10-ft^3 receiver until a pressure of 200 lb/in.^{2} abs is attained. Determine the work required for an adiabatic process with (*a*) nothing in the receiver at the beginning of the process, (*b*) H_2O at the supply conditions in the receiver at the beginning of the process.

CHAPTER VI

MIXTURES OF MEDIUMS

COORDINATES

Perfect Gases.—The molecules of each substance in a mixture of mediums in the perfect-gas state occupy or are uniformly distributed throughout the *entire volume* of the mixture. The molecules of each substance exert a pressure on the walls of the container, the *total pressure* being the sum of the pressures exerted by the molecules of each constituent of the mixture. The pressure exerted by each constituent is called its *partial pressure.* Thus

$$P = P_1 + P_2 + P_3 + \cdots P_n \quad (1)$$

which is known as *Dalton's Partial Pressure Law* (see Fig. 53).

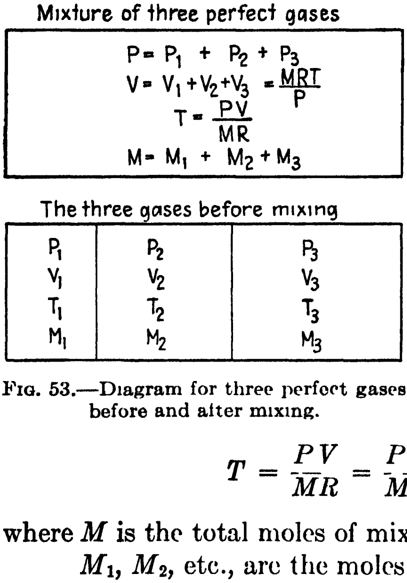

FIG. 53.—Diagram for three perfect gases before and after mixing.

The temperature, pressure, or volume of a gaseous mixture may be evaluated from the Equation of State. Thus,

$$T = \frac{PV}{MR} = \frac{P_1V}{M_1R} = \frac{P_2V}{M_2R} \cdots \frac{P_nV}{M_nR} \quad (2)$$

where M is the total moles of mixture constituents,

M_1, M_2, etc., are the moles of each constituent,

and R is the Universal Gas Constant.

It is obvious that

$$M = M_1 + M_2 + M_3 \ldots M_n \quad (3)$$

and, from Eq. (2) it follows that the pressures are directly proportional to the moles. Thus,

$$\frac{P_1}{P} = \frac{M_1}{M}, \quad \frac{P_2}{P} = \frac{M_2}{M}, \text{ etc.} \quad (4)$$

Example.—Carbon dioxide and carbon monoxide are to be mixed in the ratio of 3 to 1 by weight. The total pressure is to be 14.7 lb/in.^{2} and the temperature 500°R. Determine the volume per pound of mixture and the partial pressures of each constituent.

One pound of mixture will have 0.75 lb of CO_2 and 0.25 lb of CO.

$$\text{Moles of } CO_2 = \frac{0.75}{44} = 0.01704$$

$$\text{Moles of } CO = \frac{0.25}{28} = 0.00893$$

$$\text{Moles of mixture} = \text{sum} = 0.02597$$

$$\text{Total volume } V = \frac{MRT}{P} = \frac{0.02597 \times 1545 \times 500}{14.7 \times 144} = 9.48 \text{ ft}^3$$

$$P_{CO_2} = P\frac{M_{CO_2}}{M} = 14.7 \times \frac{0.01704}{0.02597} = 9.65 \text{ lb/in.}^2$$

$$P_{CO} = 14.7 - 9.65 = 5.05 \text{ lb/in.}^2$$

Actual Gases.—The deviation of mixtures of gases from the perfect-gas relationship is determined most simply by the use of the compressibility factor or its related factor, the residual volume. Compressibility factors and residual volumes have been determined for various gaseous mixtures* such as the methane-carbon-dioxide system (Table XXIII, Appendix).

The relation between the coordinates and the compressibility factor for a gaseous mixture is

$$P_m V_m = M_m Z_m R T_m \tag{1}$$

where subscript m indicates mixture.

One method† of evaluating Z_m is to evaluate the compressibility factor for each constituent at mixture pressure and temperature, multiply each by its respective moles, and add the results. Thus, at mixture pressure and temperature, P_m and T_m, respectively,

$$M_m Z_m = M_1 Z_1 + M_2 Z_2 \tag{2}$$

Example.—One mole of a mixture of CH_4 and CO_2, with 35.83 per cent CH_4 by weight, is to be compressed into a volume of 1.5 ft^3. The final temperature is to be 100 F. Determine the final pressure.

The compressibility factor depends on the pressure as well as the temperature. Consequently, the pressure of the mixture must be determined by trial. Assuming 5000 lb/in.^{2} as the pressure, $Z_m = 0.8584$ (Table XXIII, Appendix). Then

$$P_m = 1 \times 0.8584 \times 1{,}545 \times 560/1.5 = 4{,}950 \text{ lb/in.}^2$$

Obviously, the pressure is slightly below 4,950 lb/in.^{2} since Z_m is lower at 4,950 than at 5,000 lb/in.^{2}

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* *Industrial and Engineering Chemistry*, 1934 to date; see the work of B. H. Sage, W. N. Lacy, *et al.*, at California Institute of Technology.

† DODGE, B. F., "Chemical Engineering Thermodynamics," p. 193, McGraw-Hill Book Company, Inc., New York, 1944.

The compressibility factors for the pure substances at the same assumed pressure and at 100 F are

$$Z_{CH_4} = 0.9813 \qquad Z_{CO_2} = 0.624$$

Also, $0.3583/16 = 0.0224$ mole of CH_4/lb of mixture
and $0.6417/44 = \underline{0.0146}$ mole of CO_2/lb of mixture
Sum $= 0.0370$ mole of mixture/lb of mixture

Then, $0.0224/0.0370 = 0.605$ mole of CH_4/mole of mixture
and $0.0146/0.0370 = 0.395$ mole of CO_2/mole of mixture
From Eq. (2), $Z_m = 0.605 \times 0.9813 + 0.395 \times 0.624 = 0.840$

This value is about 2 per cent less than the experimental value for the mixture.

Reduced coordinates may be used to evaluate the compressibility factors for mixtures when experimental data even for the pure substances are not available. The Law of Corresponding States (that all gases act alike when in the same state referred to the critical conditions) indicates that the compressibility of all gases is approximately the same at the same reduced pressure and temperature. Thus, approximate compressibility factors may be obtained from Charts F and G, Appendix.

Example.—Determine the compressibility factor at 5,000 lb/in.^{2} and 100 F for the mixture in the preceding example.

The critical coordinates for CH_4 and CO_2 (Table IX, Appendix) are

	T_c, °R	P_c, lb/in.^{2}
CH_4	343	673
CO_2	547	1,071

The reduced coordinates are

	T_r	P_r
CH_4	$560/343 = 1.63$	$5{,}000/673 = 7.43$
CO_2	$560/547 = 1.02$	$5{,}000/1{,}071 = 4.66$

From Chart F, Appendix, at $P_r = 7.43$ and $T_r = 1.63$, $Z_{CH_4} = 1.02$. This compares with 0.9813 determined experimentally. Also, at $P_r = 4.66$ and $T_r = 1.02$, $Z_{CO_2} = 0.62$. This compares with 0.624 also determined experimentally. Then

$$Z_m = 0.605 \times 1.02 + 0.395 \times 0.62 = 0.86$$

This compares with 0.8584 determined experimentally. However, it should be noted that such correlation is not obtained with all mixtures.[*]

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[*] DODGE, *op. cit.*, p. 160.

Perfect-gas and Saturated-vapor Mixtures.—The pressure exerted by a saturated vapor alone depends on its temperature. In mixture with a perfect gas, the temperature of the mixture indicates the pressure of the saturated vapor the same as when alone. Then

$$P_{\text{mix}} = P_{\text{vapor}} + P_{\text{gas}} \tag{1}$$

The volume of each constituent is the mixture volume. Hence, the solution for V_{mix} depends on the data available.

Example.—One pound of saturated water vapor and 1 lb of air occupy a given volume at 180 F. Determine the volume occupied and the total pressure of the mixture.

From Table VI, Appendix, at 180 F

$$P_{wv} = 7.510 \text{ lb/in.}^2 \qquad \text{and} \qquad V_g = 50.23 \text{ ft}^3$$

The volume of 50.23 ft^3 occupied by 1 lb of water vapor at its partial pressure is also the volume occupied by the 1 lb of air at its partial pressure

$$\text{Thus,} \qquad P_{\text{air}} = \frac{M_{\text{air}}RT}{V} = \frac{1}{28.97} \times \frac{1{,}545 \times 640}{144 \times 50.23} = 4.73 \text{ lb/in.}^2$$

$$\text{and total pressure,} \quad P = P_{wv} + P_{\text{air}} = 7.51 + 4.73 = 12.24 \text{ lb/in.}^2$$

If one of the constituents is in the liquid-vapor region, its partial pressure is a function of the mixture temperature, but one of the coordinates or properties x, V, S, U, or H must be known to determine the volume. The volume of the saturated vapor is the volume of the gaseous constituent since the gas can occupy only a negligible part of the volume occupied by the liquid.

Example.—A mixture of air and H_2O having a quality of $x = 0.5$ is at a temperature of 200 F. Determine the pounds of air per pound of H_2O if the total pressure is 50 lb/in.^{2}

From Table VI, Appendix, at $T = 200$ F,

$$P_{wv} = 11.526 \text{ lb/in.}^2 \qquad V_f = 0.01663 \text{ ft}^3 \qquad V_g = 33.64 \text{ ft}^3$$

$$\text{Volume of saturated liquid} = (1 - x)V_f = (1 - 0.5)0.01663 = 0.008$$

$$\text{Volume of saturated vapor} = xV_g = 0.5 \times 33.64 = 16.82 \text{ ft}^3$$

$$P_{\text{air}} = P - P_{wv} = 50 - 11.526 = 38.47 \text{ lb/in.}^2$$

$$\text{Then,} \qquad M_{\text{air}} = \frac{P_{\text{air}}V}{RT} = \frac{38.47 \times 144 \times 16.82}{1{,}545 \times 660} = 0.0915 \text{ mole} = 2.65 \text{ lb}$$

The vapor may be superheated, in which case two of the coordinates or properties as well as the quantity of medium must be known to determine the condition of the vapor.

Example.—One pound of air and 1 lb of H_2O occupy a volume of 16.897 ft^3 at a temperature of 400 F. Determine the total pressure.

From Table VI, Appendix, at 400 F, $V_g = 1.86$ ft^3. This is smaller than the volume of the mixture which is the volume of the vapor, indicating that the H_2O is superheated.

From Table VIII, Appendix, at 400 F, $V = 16.897$ ft^3 when $P = 30$ lb/in.^{2}

Then. $$P_{\text{air}} = \frac{M_{\text{air}}RT}{V} = \frac{1}{28.97} \cdot \frac{1{,}545 \times 860}{144 \times 16.897} = 18.9 \text{ lb/in.}^2$$

$$\text{Total pressure} = P_{wv} + P_{\text{air}} = 30 + 18.9 = 48.9 \text{ lb/in.}^2$$

Humidity; Air and Water Vapor.—The amount of water vapor, or any other vapor, that can be contained in a mixture with air varies from zero up to the quantity of saturated vapor at mixture temperature that will occupy the same volume as that occupied by the air. All quantities of water vapor less than the maximum that the mixture can contain are superheated at mixture temperature under stable equilibrium conditions, the water-vapor pressure being that required for a vapor volume equal to that of the mixture.

The *absolute* humidity of air is defined as the quantity of water vapor, whether saturated or superheated, in 1 ft^3 of mixture of air and water vapor. The maximum absolute humidity at any temperature is the reciprocal of the specific volume of saturated water vapor ($1/V_g$) at that temperature.

Example.—The maximum humidity of air at 100 F would be

$$1/350.4 = 0.00285 \text{ lb water vapor/ft}^3 \text{ mixture}$$

Obviously, the maximum humidity increases with an increase in temperture since V_g decreases.

The *relative* humidity is the ratio of the absolute humidity of air at a given temperature to the maximum absolute humidity of air at the same temperature. The relative humidity of air when saturated is 100 per cent regardless of the temperature.

Example.—Determine the absolute humidity of air at 100 F if the relative humidity is 50 per cent

At 100 F and 100 per cent relative humidity the air is saturated and contains 0.00285 lb water vapor/ft^3 mixture. Then,

$$\text{Absolute humidity} = 0.00285 \times 0.50 = 0.00143 \text{ lb } H_2O \text{ vapor/ft}^3 \text{ mixture}$$

Relative humidities, lower than 100 per cent, indicate a superheated condition for the water vapor. This is indicated by a point B on the T-S diagram (Fig. 54) for H_2O, located at the same temperature as the mixture but at a lower pressure than that corresponding to the saturated condition. The specific volume and temperature of the superheated H_2O vapor indicate the pressure of the H_2O vapor. However, superheated vapor tables are not available for the low pressures usually encountered in air conditioning. Examination of the superheated region of any H_2O diagram in the neighborhood of 100 F indicates that water vapor at this condition acts very nearly as a perfect gas, since enthalpy lines are practically parallel with temperature lines. Thus, since points A and B (Fig. 54) are at the same temperature, the Equation of State for a perfect gas indicates that

$$P_A V_A = P_B V_B \tag{1}$$

and

$$\frac{P_B}{P_A} = \frac{V_A}{V_B} = \frac{\text{sp wt}_B}{\text{sp wt}_A} = \text{relative humidity} \tag{2}$$

Example.—Determine the H_2O pressure for 50 per cent relative humidity at 100 F.

$$\frac{P_{50\%}}{P_{100\%}} = \text{relative humidity}$$

At 100 F the saturation pressure for water vapor is 0.95 lb/in.^{2} (Table VI, Appendix). P at 50 per cent relative humidity $= 0.95 \times 0.5 = 0.48$ lb/in.^{2}

The *specific* humidity of a mixture of air and water vapor is defined as the weight of H_2O vapor per pound of air. This property is useful in meteorological work to study the effect of variations in pressure and temperature on the condition of the H_2O in a given quantity of air.

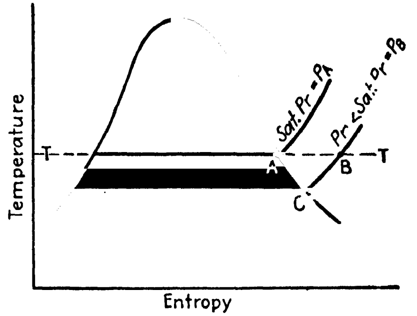

FIG. 54.—T-S diagram for H_2O.

The relative quantities of air and water vapor for any relative humidity can be determined from the volume required for 1 lb of air under the conditions of the air in the mixture. With the humidity known, the total quantity of water in the volume occupied by 1 lb of air can be determined.

Example.—Determine the specific humidity of a mixture of air and H_2O vapor at 100 F and a relative humidity of 50 per cent. Total pressure is 14.7 lb/in.^{2}
From Table VI, Appendix, $P_{wv} = 0.95$ lb/in.^{2} and $V_g = 350.4$ ft^3/lb
From the preceding example, $P_{wv} = 0.48$ lb/in.^{2} Also, specific $V_{wv} = V_g/\text{rel hum} = 350.4/0.5 = 700.8$ ft^3/lb of water vapor.

$$P_{air} = P_{total} - P_{wv} = 14.7 - 0.48 = 14.22 \text{ lb/in.}^2$$

$$V_{air} = \frac{M_{air}RT}{P_{air}} = \frac{1}{28.97} \cdot \frac{1{,}545 \times 560}{14.22 \times 144} = 14.62 \text{ ft}^3\text{/lb of air}$$

$$\text{Sp humidity} = \left(\frac{V_{wv}}{700.8}\right)_T = \left(\frac{V_{air}}{700.8}\right)_T = \frac{14.62}{700.8} = 0.0209 \text{ lb of } H_2O\text{/lb of air}$$

The cooling of a mixture of air and water vapor, with an initial relative humidity of less than 100 per cent, results in a decrease in temperature and an increase in the relative humidity, although the total of quantity

H_2O vapor remains constant. Eventually, the *dew-point* temperature is reached at which temperature the H_2O vapor in the air becomes saturated and the relative humidity is 100 per cent. Since both the air and H_2O are practically perfect gases and since the quantity of each medium remains constant during the cooling process, the partial pressures also remain constant during this process. Further cooling results in a further decrease in temperature and a condensation of some of the H_2O vapor while the relative humidity remains at 100 per cent.

Example.—Determine the dew point for air at 100 F and 14.7 lb/in.^{2} pr, with a relative humidity of 27 per cent.

From Table VI, Appendix, at 100 F, $P_{sat} = 0.95$ lb/in.^{2}

$$P_{wv}/P_{sat} = \text{relative humidity}$$

hence,

$$P_{wv} = 0.27 \times 0.95 = 0.266 \text{ lb/in.}^2$$

Cooling the mixture to the dew point and holding the pressure constant, the H_2O vapor will be saturated at the temperature corresponding to the saturation pressure of 0.266 lb/in.^{2} From Table VI, this temperature is found to be 60 F. If B (Fig. 54) represents the initial condition, C represents the dew point.

The relative humidity and water-vapor content of air are determined from wet- and dry-bulb temperatures by the use of a psychrometric chart (Chart D, Appendix. See Psychrometric Process, page 109).

Mixtures of Mediums in Liquid and Vapor Regions.—Volumetric behavior of mixtures of mediums in the liquid region may be represented by the use of the compressibility factor. Experimental data (Fig. 55) for such mixtures show a discontinuity of the slope of isotherms at the phase-boundary line. The residual volume may be found in the usual manner.

Example.—Determine the specific and residual volumes of a mixture of methane and *n*-pentane, containing a 0.3857 weight fraction of methane, at a pressure of 2,500 lb/in.^{2} and a temperature of 340 F.

In 1 lb of mixture there is 0.3857 lb of methane. Thus, moles of $CH_4 = 0.3857/16 = 0.0241$; moles of $C_5H_{12} = (1 - 0.3857)/72 = 0.0085$. Total moles $= 0.0241 + 0.0085 = 0.0326$.

Also, from Fig. 55 at 2,500 lb/in.^{2} and 340 F, $Z = 0.85$.

Then, $V = ZMRT/P = 0.85 \times 0.0326 \times 1{,}545 \times 800/2{,}500 \times 144 = 0.0952$ ft^3/lb of mixture.

Residual volume, $v = (1 - Z)V = (1 - 0.85) \times 0.0952 = 0.0143$ ft^3/lb.

The pressures and temperatures for various concentrations of ammonia in mixture with H_2O, for both vapor and liquid states, are given in Table XVIII, Appendix. The total vapor pressure for such mixtures in which the liquids are mutually soluble is less than the sum of the saturated-vapor pressures of the individual constituents at the same temperature.

PROPERTIES

Internal Energy.—The internal energy of a mixture of perfect gases at a given temperature is the sum of the internal energies of the various constituents at the same temperature.

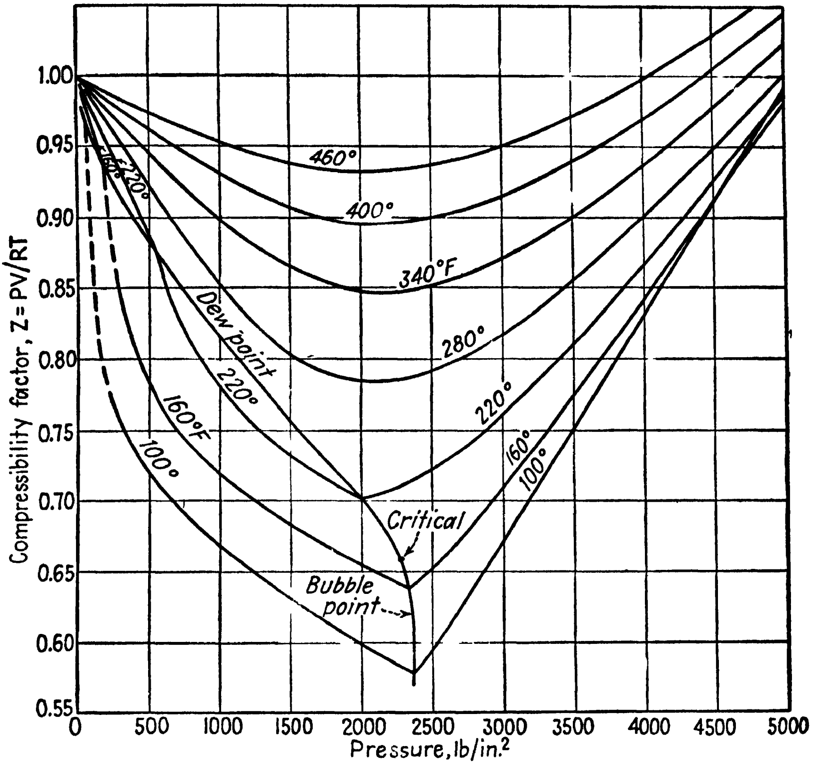

FIG 55.—Compressibility factors for a mixture of methane and n-pentane containing 0.3857 weight fraction of methane. (*B. H. Sage, H. H. Reamer, R. H. Olds, and W. N. Lacey, Phase Equilibria in Hydrocarbon Systems, Ind. & Eng. Chem.*, **34**, 1108, 1942.)

Example.—One mole of CO_2 is to be mixed with 1 mole of CH_4, both at a temperature of 140 F. Determine the internal energy of the mixture assuming perfect-gas conditions.

From Table XIX, Appendix, at 600°R,

$$U_{CO_2} = 570 \text{ Btu/mole} \qquad U_{CH_4} = 545 \text{ Btu/mole}$$

$$U_{\text{mix}} \text{ at } 600°\text{R} = 570 + 545 = 1115 \text{ Btu/2 moles of mixture}$$

For actual gases the internal energy varies with the specific volume [Eq. (C) Appendix.] Hence, the internal energy for each constituent should be evaluated for perfect-gas conditions and a correction made to the sum to account for the effect of volume on internal energy.

When the mixing of several substances at a given temperature results in a change in temperature, chemical energy is being either liberated or absorbed in a manner similar to that of a reaction, provided no other energy effects occur. The Energy Equation for the constant-volume adiabatic mixing process is

$$C_{A+B} + (U_A + U_B)_{T_1} = (U_{A+B})_{T_2} \qquad (1)$$

where A and B indicate the two constituents being mixed.

If T_2 is greater than T_1, heat must be transferred out of the resulting mixture to return it to the original temperature. Thus Eq. (1) becomes

$$C_{A+B} + (U_A + U_B)_{T_1} = (U_{A+B})_{T_1} + Q_{\text{out}} \qquad (2)$$

in which case Q_{out} is the heat of solution, dilution, or reaction for constant-volume mixing.* Heats of solution, etc., are determined experimentally, and usually $(U - C)_{A+B}$ is evaluated and designated as the internal energy of the mixture.

Enthalpy.—The enthalpy of a mixture of perfect gases at a given temperature is the sum of the enthalpies of the various constituents at the same temperature. For actual mediums the enthalpy varies with pressure as indicated in the Appendix.

When the mixing of several substances at a given temperature results in a change in temperature, chemical energy is being either liberated or absorbed in a manner similar to that of a reaction, provided no other energy effects occur. The Energy Equation for the steady-flow adiabatic mixing process is

$$C_{A+B} + (H_A + H_B)_{T_1} = (H_{A+B})_{T_2} \qquad (1)$$

where A and B are the constituents being mixed.

If T_2 is higher than T_1, heat must be transferred out of the resulting mixture to return it to the original temperature. Thus, Eq. (3) becomes

$$C_{A+B} + (H_A + H_B)_{T_1} = (H_{A+B})_{T_1} + Q_{\text{out}} \qquad (2)$$

in which case Q_{out} is the heat of solution, dilution, or reaction. Heats of solution, etc., are determined experimentally, and usually $(H - C)_{A+B}$ is evaluated and designated as the enthalpy of the mixture. Enthalpy (or internal-energy) evaluation in this manner includes any effect of pressure change on enthalpy.

Enthalpy-concentration diagrams and tables of data have been prepared for various liquid and vapor mixtures such as ammonia and water (Table XVIII, Appendix).

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* Usually constant-pressure or steady-flow processes are used to evaluate heats of solution.

Example.—Liquid H_2O and ammonia are mixed at 100 F in such proportions that the final mixture concentration is 0.377. Determine the heat of solution.

From Table VI, Appendix, $H_f = 68.0$ Btu/lb of H_2O
From Table IX, Appendix, $H_f = 155.2$ Btu/lb of NH_3
From Table XVIII, Appendix, $H_{mix} = -5$ Btu/lb of mixture
Substituting in Eq. (2), modified as indicated,

$$0.377 \times 155.2 + 0.623 \times 68.0 = 1 \times (-5) + Q_{out}$$

or

$$Q_{out} = 105.9 \text{ Btu}$$

$$\text{Heat of solution} = 105.9/0.377 = 281 \text{ Btu/lb of } NH_3$$

Entropy.—The entropy of a perfect gas is given by the expression

$$S = \int_{T_0}^{T} c_V \frac{dT}{T} + R \ln \frac{V}{V_0} + S_{0_{T,V}} \quad \text{Eq. (18), p. 56} \qquad (1)$$

or

$$S = \int_{T_0}^{T} c_P \frac{dT}{T} - R \ln \frac{P}{P_0} + S_{0_{T,P}} \quad \text{Eq. (25), p. 56} \qquad (2)$$

Tables XXI and XXII, Appendix, contain values of $\int c_V dT/T$ and $\int c_p dT/T$ above a datum temperature of $T_0 = 520°R$.

Any volume or pressure may be assumed to be a datum value, in which case the volume or pressure term is eliminated. The third term may be eliminated if no reaction occurs in the process. Thus, the values in Tables XXI and XXII may be used as the entropies of a medium. Obviously, these are not absolute values because of the temperature datum plane and since S_0 is not included. However, T_0 and S_0 are eliminated in evaluating differences of entropy for a given gas.

The mixing or diffusion of several perfect gases initially at pressure P and temperature T, by connecting the several containers of the gases, results in the same total pressure and temperature for the mixture. However, each gas in mixing has its pressure reduced to its partial pressure. Thus, after mixing, the entropy for each gas is

$$S = \int_{T_0}^{T} c_P \frac{dT}{T} - R \ln pp + S_{0T,P} \qquad (3)$$

in which pp is the partial pressure of each gas.

The entropy of the mixture is the sum of the entropies of each constituent at its condition in the mixture. Thus,

$$S_{mix} = S_1 + S_2 + \cdots + S_n \qquad (4)$$

Example.—One mole of CH_4 and 0.651 moles of CO_2, each at a pressure of 1 atm and a temperature of 160 F, are mixed. The final pressure is 1 atm. Determine the entropy of the constituents before and after mixing, assuming perfect-gas relationships.

From Table XXII, Appendix, at 620°R, since P and T are given,

$$\int c_P \frac{dT}{T} \text{ for } CH_4 = 1.55 \text{ Btu/(mole} \times {}^\circ\text{R)} \qquad \int c_P \frac{dT}{T} \text{ for } CO_2 = 1.59 \text{ Btu/(mole} \times {}^\circ\text{R)}$$

Also, $R \ln P = 0$ assuming the value of $P = 1$ atm to be a unit pressure.

Then, before mixing,

$$\Sigma S_{\text{before}} = S_{CH_4} + S_{CO_2} = 1 \times 1.55 + 0.651 \times 1.59 = 2.585 \text{ Btu/}^\circ\text{R}$$

The mixture contains 1.651 moles of gas of which 1 mole is CH_4.

$$\begin{aligned} pp\ CH_4 &= M_{CH_4}/M_{\text{total}} = 0.605 \text{ atm} \\ pp\ CO_2 &= M_{CO_2}/M_{\text{total}} = 0.395 \text{ atm} \\ R \ln pp &= 1.986 \ln 0.605 = -0.998 \text{ for 1 mole of } CH_4 \\ R \ln pp &= 1.986 \ln 0.395 = -1.845 \text{ for 1 mole of } CO_2 \\ S_{CH_4} &= 1 \times (1.550 + 0.998) = 2.548 \text{ Btu/}^\circ\text{R} \\ S_{CO_2} &= 0.651 \times (1.590 + 1.845) = 2.236 \text{ Btu/}^\circ\text{R} \end{aligned}$$

$$\Sigma S_{\text{mixture}} = S_{CH_4} + S_{CO_2} = 4.784 \text{ Btu/}^\circ\text{R}$$

The entropy change for the mixing process is

$$\Sigma(-MR \ln pp), \text{ or } 0.998 + 0.651 \times 1.845 = 2.199 \text{ Btu/}^\circ\text{R}$$

The foregoing example indicates that the mixing or diffusion of perfect gases is not an ideal process since there is an increase in entropy even though the process is adiabatic. The increase in entropy because of diffusion of gases loses its significance when the two gases are the same. This is often referred to as the *Gibbs paradox.*

PROCESSES

The method of analysis and the solution of processes dealing with mixtures are the same as used with a single medium. Consequently, only a few nonflow and typical steady-flow processes will be illustrated. Also, considerable attention will be given to mixtures of air and water vapor because of the relation to air conditioning.

Constant-volume Process.—The Energy Equation for the constant-volume heating process is

$$U_1 + Q_{\text{in}} = U_2 \tag{1}$$

and for the cooling process

$$U_1 = U_2 + Q_{\text{out}} \tag{2}$$

in which the energy terms refer to the mixture.

Example.—A mixture containing a weight fraction of 0.3583 of CH_4 in CO_2 is cooled at constant volume from a pressure of 6,000 lb/in.² and a temperature of 400 to 100 F. Determine the final pressure and heat removed per mole of mixture.

Assuming perfect-gas relations and noting $V_2 = V_1$,

$$P_2 = P_1V_1T_2/V_2T_1 = 6{,}000 \times 560/860 = 3{,}910 \text{ lb/in.}^2$$

From Table XIX, Appendix, U_{CH_4} at 860°R = 2599 Btu/mole. U_{CO_2} at 860°R = 2,627 Btu/mole. U_{CH_4} at 560°R = 271 Btu/mole. U_{CO_2} at 560°R = 280 Btu/mole.

A weight fraction of 0.3583 of CH_4 is equivalent to a 0.605 mole fraction of CH_4 in mixture with CO_2.

Substituting in Eq. (2), in the following form,

$$[(MU)_{CH_4} + (MU)_{CO_2}]_{920} = [(MU)_{CH_4} + (MU)_{CO_2}]_{560} + Q_{out}$$

$$0.605 \times 2599 + 0.395 \times 2627 = 0.605 \times 271 + 0.395 \times 280 + Q_{out}$$

and $$Q_{out} = 2335 \text{ Btu}$$

Nonflow Isothermal Process.—This process might occur in a cylinder, heat being added or abstracted to maintain constant temperature while work is done by or on the medium, respectively. For an expansion of the medium

$$U_1 + Q_{in} = U_2 + W_{out} \tag{1}$$

and for a compression process

$$U_1 + W_{in} = U_2 + Q_{out} \tag{2}$$

If one of the constituents of the mixture is in the perfect-gas region, its internal energy remains constant during the process. Also, the heat transferred is evaluated more readily than the work since

$$Q_{in} = T(S_2 - S_1) \qquad \text{or} \qquad Q_{out} = T(S_1 - S_2) \tag{3}$$

Example.—A mixture of 1 lb of air and 1 lb of H_2O is at a temperature of 300 F. The quality of the H_2O is 0.5. An isothermal change takes place in an engine cylinder until the volume of the mixture is increased to five times the initial volume. Determine the work done.

The initial conditions are determined as follows:

From Table VI, Appendix, at 300 F, P_{wv} = 67.01 lb/in.², V_f = 0.0175 ft³, V_{fg} = 6.449 ft³, and V_g = 6.466 ft³/lb.

$$V_1 = V_x = V_f + xV_{fg} = 0.0175 + 0.5 \times 6.449 = 3.242 \text{ ft}^3\text{/lb wv}$$

also, $$U_x = U_f + xU_{fg} = 269.1 + 0.5 \times 830.1 = 684.2 \text{ Btu/lb wv}$$

and $$S_x = S_f + xS_{fg} = 0.4369 + 0.5 \times 1.1980 = 1.0359 \text{ Btu/(lb} \times \text{°R)}$$

The air occupies the same volume as the water vapor. Hence,

$$V = V_{wv} = xV_g = 0.5 \times 6.466 = 3.233 \text{ ft}^3$$

$$P_{air} = \frac{MRT}{V} = \frac{1}{28.97} \times \frac{1{,}545 \times 760}{3.233 \times 144} = 87.1 \text{ lb/in.}^2$$

and $$P_1 = P_{wv} + P_{air} = 67.0 + 87.1 = 154.1$$

The final conditions are determined as follows:

$$V_2 = 5 \times V_1 = 5 \times 3.242 = 16.21 \text{ ft}^3$$

Inspection of Table VIII, Appendix, shows that 1 lb of H_2O at 300 F and a volume of 16.21 ft³ is superheated and has the following conditions:

$$P_{wv} = 27.5 \text{ lb/in.}^2 \qquad S_{wv} = 1.7439 \text{ Btu/(lb} \times {}^\circ\text{R)} \qquad U_{wv} = 1107.3 \text{ Btu/lb}$$

The Water Constituent

$$Q_{in} = T\,\Delta S = 760(1.7439 - 1.0359) = 538.1 \text{ Btu/lb}$$

The Air Constituent

From Eq. (17), page 56,

$$S_2 - S_1 = \int c_V \frac{dT}{T} + R \ln \frac{V_2}{V_1}$$

and, since T is constant, $= 1.986 \ln 5 = 3.193$ Btu/mole

Then, $Q_{in} = T\,\Delta S = 760 \times 3.193 = 2426.7$ Btu/mole $= 84.3$ Btu/lb of air

The Mixture

Substituting in Eq. (1), modified as follows:

$$(U_{air} + U_{wv})_1 + Q_{in} = (U_{air} + U_{wv})_2 + W_{out}$$

and, since U_{air} is constant,

$$684.2 + (538.1 + 84.3) = 1107.3 + W_{out}$$
$$W_{out} = 199.3 \text{ Btu}$$

Non-flow Adiabatic Isentropic Process.—This process may occur in an engine or compressor cylinder and may involve either expansion or compression of the mediums. The Energy Equations for the two processes are

$$U_1 = U_2 + W_{out} \tag{1}$$

and

$$U_1 + W_{in} = U_2$$

Since the process is isentropic,

$$S_1 \text{ of mixture} = S_2 \text{ of mixture}$$

and the internal-energy values of Eqs. (1) and (2) must be evaluated at the same entropy.

Example.—A mixture containing a weight fraction of 0.3583 CH_4 in CO_2 at a pressure of 6,000 lb/in.² and a temperature of 400 F is expanded adiabatically and isentropically to a temperature of 100 F. Determine the final condition and the work done per mole of mixture.

Perfect-gas Solution

In 1 mole of the mixture there will be 0.605 mole of CH_4. (see example, page 106).

Then,

$$\text{pp of } CH_4 = 0.605 \times 6{,}000 = 3{,}630 \text{ lb/in.}^2 = 247.0 \text{ atm}$$
$$\text{pp of } CO_2 = 0.395 \times 6{,}000 = 2{,}370 \text{ lb/in.}^2 = 161.3 \text{ atm}$$

From Table XXII, Appendix, at 860°R, using the table values for a pressure of 1 atm,

$$S_{CH_4} = 0.605(4.78 - 1.986 \ln 247.0) = -3.73 \text{ Btu/}^\circ\text{R}$$
$$S_{CO_2} = 0.395(4.84 - 1.986 \ln 161.3) = -2.08 \text{ Btu/}^\circ\text{R}$$
$$S_1 \text{ of mixture} = -5.81 \text{ Btu/}^\circ\text{R}$$

From Table XIX, Appendix, at 860°R,

$$U_{CH_4} = 0.605 \times 2599 = 1572 \text{ Btu}$$
$$U_{CO_2} = 0.395 \times 2627 = \underline{1038} \text{ Btu}$$
$$U_1 \text{ of mixture} = 2610 \text{ Btu}$$

An estimate of the final pressure may be obtained by applying Eq. (9), page 73, to the process. Assuming a value of k of 1.3 which is indicated from specific heat values, the estimated final pressure is about 900 lb/in.²

Assuming several values for the final pressure, the solution is made as follows.

At 560°R, $\int c_p dT/T$ for CH_4 = 0.70 and for CO_2 = 0.67 Btu/(mole × °R) (Table XXII, Appendix).

Assume P_2	40 atm	50 atm	60 atm
Partial pressure of CH_4, atm	24.20	30.25	36.30
Partial pressure of CO_2, atm	15.80	19.75	23.40
$R \ln pp$ CH_4	6.33	6.77	7.13
$R \ln pp$ CO_2	5.48	5.92	6.26
S of $CH_4 = \int c_p dT/T - R \ln pp$	−5.63	−6.07	−6.43
MS of CH_4	−3.41	−3.67	−3.89
S of $CO_2 = \int c_p dT/T - R \ln pp$	−4.81	−5.25	−5.59
MS of CO_2	−1.90	−2.07	−2.21
S_2 of mixture	−5.31	−5.74	−6.10

Plotting S_2 of mixture against assumed P_2 results in a solution at P_2 = 51.7 atm.

From Table XIX, Appendix, at 560°R,

$$U_{CH_4} = 0.605 \times 271 = 164 \text{ Btu}$$
$$U_{CO_2} = 0.395 \times 280 = \underline{111} \text{ Btu}$$
$$U_2 \text{ of mixture} = 275 \text{ Btu}$$

Substituting in Eq. (1), page 108,

$$2610 = 275 + W_{out}$$

or

$$W_{out} = 2335 \text{ Btu}$$

Psychrometric Process.—The adiabatic, steady-flow saturation of a mixture of air and vapor by spraying an additional amount of the medium in the liquid state into the air stream results in a final temperature known as the *thermodynamic wet-bulb temperature,* provided the liquid sprayed is at this resulting temperature.

Some of the unsaturated air that flows over the wet-bulb thermometer mixes with the H_2O vapor forming from the wick around the thermometer bulb and leaves in a saturated condition. The evaporation of the H_2O reduces the temperature of the liquid H_2O and the mixture of H_2O vapor and air that is saturated. The wet-bulb temperature indicates the effect of the evaporation process on the leaving mixture.

The Energy Equation for the process, with H_2O as the saturating medium, is

$$(H_{\text{mix}})_{T_1} + (H_{\text{water}})_{T_2} = (H_{\text{sat mix}})_{T_2} \tag{1}$$

or

$$(H_{\text{air}} + M_1H_{\text{wv}})_{T_1} + (M_wH_w)_{T_2} = (H_{\text{air}} + M_2H_{\text{wv}})_{T_2} \tag{2}$$

in which the dimensions are per unit quantity of air, and M_1 and M_2 are the quantities of H_2O vapor per unit quantity of air before and after the air has been saturated, respectively.

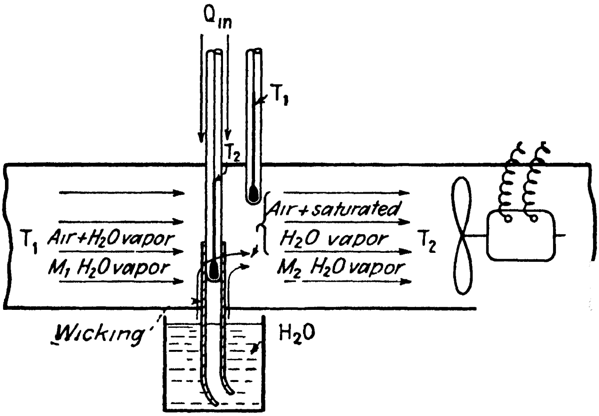

FIG 56 —Wet- and dry-bulb psychrometer.

Example.—Determine the thermodynamic wet-bulb temperature for 100 F air having a relative humidity of 50 per cent Check the result with the value obtained from the psychrometric Chart D, Appendix.

From Table VI, Appendix, at 100 F,

$$P_{\text{wv}} = 0.95 \text{ lb/in.}^2 \quad \text{and} \quad V_g = 350.4 \text{ ft}^3$$

At 50 per cent relative humidity, $P_{\text{wv}} = 0.5 \times 0.95 = 0.48$ lb/in.² and $V_{\text{wv}} = 350.4 \div 0.5 = 700.8$ ft³/lb.

$$V_{\text{air}} = \frac{MRT}{P_{\text{air}}} = \frac{1 \times 1545 \times 560}{144(14.7 - 0.48)} = 422.5 \text{ ft}^3\text{/mole of air}$$

Wt of wv/mole of air $= M_1 = V_{\text{air}} \div V_{\text{wv}} = 422.5 \div 700.8 = 0.602$ lb

Eq. (2) may be written

$$(H_{\text{air}} + M_1H_{\text{wv}})_{T_1} = (H_{\text{air}} + M_2H_{\text{wv}})_{T_2} - (M_wH_w)_{T_2}$$

The left-hand side of the equation is evaluated as follows:

From Table XIX, Appendix, at 560°R,

$$H_{\text{air}} = 1308 \text{ Btu}$$

From Table VI, Appendix, at 100 F,

$$M_1H_{\text{wv}} = 0.602 \times 1105.2 = 665 \text{ Btu}$$

$$(H_{\text{air}} + M_1H_{\text{wv}})_{100^\circ} = 1308 + 665 = 1973 \text{ Btu}$$

The right-hand side of the equation is evaluated at various temperatures until an equality with the left-hand side is obtained Thus,

Assume T_2	80 F	83 F	85 F
P of sat wv	0.51	0.56	0.60
V_g	633.1	577.4	543.5
$V_{air} = MRT_2/P_{air}$	408	412	414
$M_2 = V_{air} \div V_g$	0.645	0.714	0.762
$M_w = M_2 - M_1$	0.043	0.112	0.160
$-M_wH_w$, Btu	−2	−6	−8
H_{air}, Btu	1169	1190	1204
M_2H_{wv}, Btu	707	784	838
Right side = sum	1874	1968	2034

T_2 is found to be about 83.2 F. The intersection of the 100 F dry-bulb temperature line on Psychrometric Chart D, Appendix, with the relative-humidity line of 50 per cent checks very nearly the computed wet-bulb temperature.

The wet-bulb thermometer of the psychrometer (Fig. 56), when used for air and H_2O mixtures, indicates approximately the thermodynamic wet-bulb temperature, the deviation from the true value depending on variations in instrument design and operating conditions. Obviously, heat-transfer effects would cause some deviation in the temperature of the liquid H_2O supplied and in the indication of the wet-bulb thermometer.*

Subtracting $(M_1H_w)_{T_2}$ from both sides of Eq. (2) results in

$$(H_{mix})_{T_1} - (M_1H_w)_{T_2} = (H_{mix})_{T_2} - (M_2H_w)_{T_2} \tag{3}$$

This relation indicates that the enthalpy of the mixture of air and water vapor at any condition minus the enthalpy of the liquid or solid at the dew-point temperature for the given condition is constant for any thermodynamic wet-bulb line on the psychrometric chart. Carrier and Mackey† called attention to the constancy of this function and termed it ΣH. Obviously,

$$H_{mix} = \Sigma H + M_{wv} (H_{f \text{ or } i})_{t \text{ wet bulb}} \tag{4}$$

Practically, the enthalpy values at saturation may be used for the wet-bulb lines as was done on the psychrometric chart developed by Urban in 1935. See Chart D of the first edition of this book. However, Palmatier and Wile‡ have added contours of the deviation from the saturation value of enthalpy (Chart D, Appendix) and have tabulated the corrections for M_{wv} and H for barometric pressures other than 29.92 in. Hg.

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* Arnold, J. H., The Theory of the Psychrometer, *Physics*, **4**, 255, 334 (1933). Wile, D. D., Psychrometry in the Frost Zone, *Refrig. Eng.*, October, 1944.

† Carrier, W. H., and C. O. Mackey, A Review of Existing Psychrometric Data in Relation to Practical Problems, *Trans. A.S.M.E.*, **59**, 33 (1937).

‡ Palmatier, E. P., and D. D. Wile, A New Psychrometric Chart, *Refrig. Eng.*, **52**, 31 (1946).

Air-conditioning Process.—Air conditioning consists of changing the temperature and humidity of atmospheric air to some desired condition. This is accomplished usually in a steady-flow process (Fig. 57) in which the atmospheric air is inducted into one end of the system and discharged from the other end at the desired condition. Usually, total pressure differences are negligible and the process is practically one of constant pressure. The process is divided into two parts:

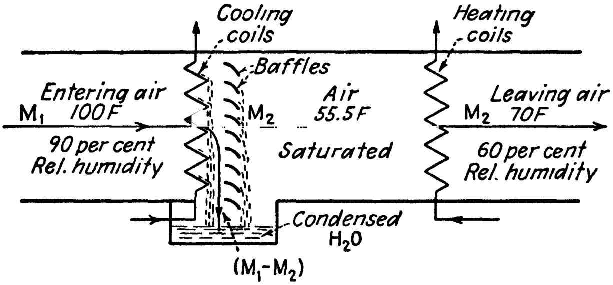

FIG. 57.—Elementary air-conditioning apparatus.

1. The temperature of the air is changed to the dew-point temperature of the desired condition and the air is saturated with water vapor. If cooling is required, the air will be saturated in some cases before the dew point is reached and some water vapor will have been removed. If heating is required, sufficient H_2O vapor must be added to make the air saturated at the dew point.

2. The air at the dew-point temperature (saturated with water vapor) is heated at constant pressure to the desired final condition.

Example.—It is desired to supply air at 70 F and 60 per cent relative humidity to a given factory room. Determine the cooling and heating requirements per mole of dry air. Atmospheric conditions are 100 F, relative humidity is 90 per cent, and the barometer is 29.5 in. Hg.

From Table VI, Appendix, $P_{wv} = 0.363$ lb/in.^{2} if saturated at 70 F. Therefore, $P_{wv} = 0.6 \times 0.363 = 0.218$ lb/in.^{2} Inspection of Table VI indicates a dew-point temperature of 55.5 F for this H_2O vapor pressure. Thus, the atmospheric air must be cooled from 100 F and 90 per cent relative humidity to 55.5 F, and any surplus H_2O must be removed.

The Cooling Process

The Energy Equation for this part of the process (Fig. 57) is

$$(H_{air} + M_1H_{wv})_{100} = (H_{air} + M_2H_{wv})_{55.5} + (M_1 - M_2)H_{f\,55.5} + Q_{out} \quad (1)$$

At 100 F, pp of air is 29.5 in. Hg × 0.491 lb/(in.² × in. Hg) − 0.9 × 0.95 lb/in.² = 13.73 lb/in.²

$$V_{air} = MRT/P = 1 \times 1545 \times 560/13.73 \times 144 = 437 \text{ ft}^3\text{/mole of air}$$

$$V_{wv} = V_g/\text{rel hum} = 350.4/0.90 = 389 \text{ ft}^3\text{/lb of } H_2O$$

Then, $M_1 = 437/389 = 1.124$ lb of H_2O/mole of air

At 55.5 F, pp of air is 29.5 × 0.491 − 0.22 = 14.37 lb/in.²

$$V_{air} = 1 \times 1545 \times 515.5/14.37 \times 144 = 385 \text{ ft}^3\text{/mole of air}$$

Then, $M_2 = V_{air}/V_g = 385/1406 = 0.274$ lb of H_2O/mole of air

From Table XIX, Appendix, at 560°R, H_{air} = 1308 Btu/mole, and at 515.5°R H_{air} = 1000 Btu/mole.

The H of the water vapor at 100 F and 90 per cent relative humidity is practically the same as that for 100 per cent relative humidity, or H_g. The required H values for the H_2O are obtained from Table VI, Appendix. Substituting in Eq. (1),

$$1308 + 1.124 \times 1105.2 = 1000 + 0.274 \times 1086.1 + (1.124 - 0.274)23.6 + Q_{out}$$

or

$$Q_{out} = 1233 \text{ Btu/mole of dry air}$$

In this process $M_1 - M_2$ or 0.850 lb of H_2O are condensed and removed from the air stream.

The Heating Process

The Energy Equation for the heating process (Fig. 57) is

$$(H_{air} + M_2H_{wv})_{55.5} + Q_{in} = (H_{air} + M_2H_{wv})_{70} \qquad (2)$$

Substituting the various values in this equation,

$$1000 + 0.274 \times 1086.1 + Q_{in} = 1100 + 0.274 \times 1092.3$$

or

$$Q_{in} = 101 \text{ Btu/mole of dry air}$$

Cooling-tower Process.—The cooling of liquid H_2O used in heat-transfer apparatus may be accomplished in cooling towers by spraying the liquid H_2O (Fig. 58) into an air stream which absorbs some heat from the H_2O and removes the vapor formed during the process. The imaginary envelope might be around the H_2O only, cutting the entering and leaving liquid (at 1 and 2 in Fig. 58) as well as the H_2O leaving the liquid (at 3). In this case the Energy Equation would be

$$H_1 = (1 - M_3)H_2 + M_3H_3 + Q_{out} \qquad (1)$$

If the imaginary envelope is around the air only, cutting the entering and leaving stream (at 1 and 2, Fig. 58), as well as the H_2O leaving the liquid at the same condition as before, the following Energy Equation is indicated:

$$M_{air}(H_{air} + M_1H_{wv})_1 + M_3H_3 + Q_{in} = M_{air}(H_{air} + M_2H_{wv})_2 \qquad (2)$$

Obviously, the liquid H_2O particles are leaving the liquid stream at various temperatures ranging from that of the entering to that of the leaving liquid. Thus, the assumption of any temperature in this range would permit a solution of the two processes but would result in a questionable value for Q_{in} which must equal Q_{out} if heat is not lost to the surroundings.

If the imaginary envelope (Fig. 58) is around the two mediums, the foregoing difficulty is eliminated and the following Energy Equation results, if no heat transfer occurs to or from the tower during the process:

$$(H_{H_2O})_1 + M_{air}(H_{air} + M_1H_{wv})_1 = (1 - M_3)(H_{H_2O})_2 + M_{air}(H_{air} + M_2H_{wv})_2 \qquad (3)$$

This may also be obtained by combining Eqs. (1) and (2), assuming that $Q_{in} = Q_{out}$. Also, Eqs. (1) and (3) are written for a unit quantity of liquid H_2O entering the process.

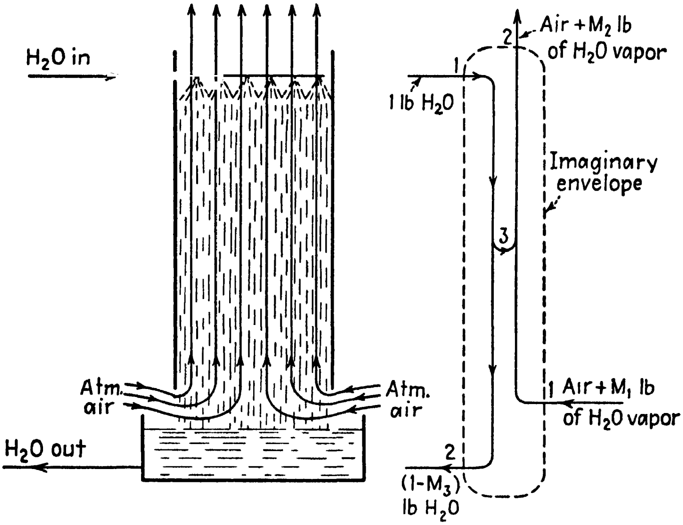

FIG. 58.—Cooling tower and flow diagram for analysis.

Obviously, the decrease in amount of liquid is the increase in amount of H_2O vapor. Thus

$$M_3 = (M_2 - M_1)M_{air} \qquad (4)$$

Example.—It is desired to cool water from 125 to 90 F in a cooling tower. The temperature of the atmosphere is 80 F, and the relative humidity is 60 per cent. The air enters the tower at such a rate that it will leave the tower at 105 F and at a relative humidity of 100 per cent. Determine the volume of air to be circulated per pound of liquid H_2O flowing into the tower.

From Table VI, Appendix, the pressure and V_g of saturated water vapor at 80 and at 105 F are 0.51 and 1.10 lb/in.², and 633.1 and 304.5 ft³/lb, respectively. Thus,

$$V_{air} \text{ at } 80 \text{ F} = 1 \times 1545 \times 540/(14.7 - 0.6 \times 0.51)144 = 403 \text{ ft}^3\text{/mole}$$

Then, $M_1 = 403/(633.1/0.60) = 0.382$ lb of H_2O/mole of air

Also, V_{air} at 105 F $= 1 \times 1545 \times 565/(14.7 - 1.1)144 = 446$ ft³/mole

and $M_2 = 446/304.5 = 1.465$ lb of H_2O/mole of air

Thus, $M_3 = (1.465 - 0.382)M_{air} = 1.083\ M_{air}$ lb

Substituting values for the H terms obtained for the air from Table XIX, and for the H_2O from Table VI, Appendix, into Eq. (3) results in

$$92.9 + M_{air}\,(1169 + 0.382 \times 1096.6) = (1 - 1.083\,M_{air})\,58.0 + M_{air}\,(1343 + 1.465 \times 1107.3)$$

and $M_{air} = 0.0257$ mole/lb entering liquid H_2O

$M_{air}\,V_{air} = 0.0257 \times 403 = 10.38$ ft^3 of atm/lb entering liquid H_2O

The *make-up* H_2O to be added to offset the loss by evaporation is $M_s = 1.083 \times 0.0257 = 0.0278$ lb/lb of entering liquid H_2O.

The height of the cooling tower required to obtain the desired cooling effect depends on the time that the air must be in contact with the H_2O spray in order to become saturated. The air may be caused to flow because of natural-draft effects or by means of fans. Thus, there are natural-draft, forced-draft, and induced-draft cooling towers.

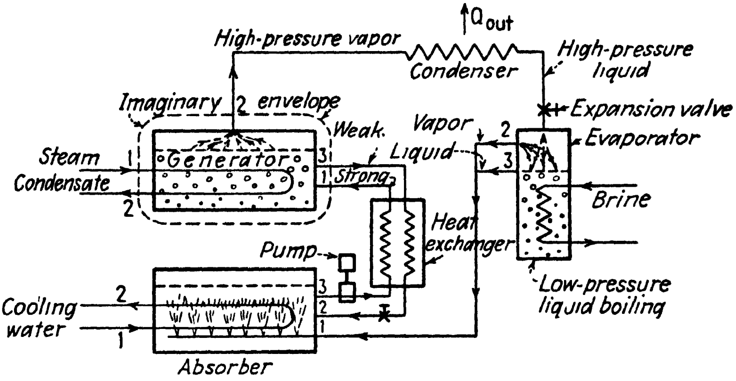

FIG. 59.—Diagrammatic sketch of NH_3-H_2O absorption refrigeration process.

Ammonia-absorption and Generation Processes.*—Water will absorb a large amount of ammonia and in so doing liberates the *heat of solution.* Similarily, if heat is added to an ammonia-water system, ammonia will be driven out of solution. These processes are used in the ammonia-water absorption-refrigeration process. The weight of ammonia in a 1 lb solution of ammonia and water is known as the concentration x. The maximum possible concentration occurs when the solution is saturated with ammonia. Increasing the pressure and decreasing the temperature increase the absorption capacity of the water (see Table XVIII, Appendix).

The ammonia is driven out of the strong solution at high pressure in the generator (Fig. 59). The high-pressure ammonia is condensed, flows through a throttling valve, as in the ammonia-compression refrigeration process (see Chap. VIII), and evaporates at a low pressure while absorbing heat. The ammonia vapor is absorbed in the absorber at low pressure by

* See "Refrigeration Data Book," *Am. Soc. Refrig. Engrs.*, 1940.

a weak solution while cooling water removes sufficient heat to maintain a constant temperature. A continuous flow of weak solution from the generator to the absorber occurs while the strong solution is pumped from the absorber to the generator.

An imaginary envelope may be thrown around any piece of apparatus in Fig. 59 and an analysis made of the steady-flow process occurring. The principle of *conservation of mass* indicates equations between the entering and leaving amounts of solutions, as well as between the entering and leaving amounts of ammonia. Data for saturated solutions with various concentrations are obtained from Table XVIII, Appendix, and with the quantity relations provide a solution for the amounts of fluids. The Energy Equation for the process provides a solution for the heating or cooling requirement.

Data for liquid solutions not saturated (subcooled) may be determined fairly accurately from the temperature and concentration, thus neglecting the effect of pressure on enthalpy. The enthalpy of superheated vapor is obtained from the ammonia and steam tables at the partial pressures indicated by the concentration. For low superheat a mean specific-heat value of $c_p = 0.55$ Btu/lb may be used to determine the increase in enthalpy above the enthalpy of the saturated mixture.

Example.—A liquid mixture of NH_3 and H_2O at 100 F and 140 lb/in.^{2} gage pr flows steadily into a generator (Fig. 59). The ammonia concentration is 0.406. Heat is added to the mixture in the generator by the condensing of saturated steam supplied at a pressure of 14.7 lb/in.^{2}, the condensate leaving at 200 F. Some of the mixture is vaporized and leaves saturated at 200 F and 140 lb/in.^{2} gage pr. The remaining portion which is a saturated-liquid mixture also flows out of the generator at 200 F and 140 lb/in.^{2} gage pr. Determine the pounds of steam supplied per pound of ammonia evaporated.

From Table XVIII, Appendix, at 100 F and $x = 0.406$,

$$x_1 = 0.406 \qquad \text{and} \qquad H_1 = -5 \text{ Btu}$$

From Table XVIII, Appendix, at 140 lb/in.^{2} gage and 200 F,

$$x_2 = 0.945 \qquad \text{and} \qquad H_2 = 732 \text{ Btu}$$

Also at 140 lb/in.^{2} gage and 200 F,

$$x_3 = 0.355 \qquad \text{and} \qquad H_3 = 108 \text{ Btu}$$

Assuming that 1 lb of medium enters the generator, for steady flow

$$M_1 = 1 \text{ lb} = M_2 + M_3 \tag{1}$$

Also, since the ammonia entering equals the ammonia leaving,

$$M_1x_1 = M_2x_2 + M_3x_3 \tag{2}$$

$$0.406 \times 1 = 0.915M_2 + 0.355M_3$$

Solving these two relations

$$M_2 = 0.087 \text{ lb} \qquad \text{and} \qquad M_3 = 0.913 \text{ lb}$$

The Energy Equation for the process is

$$(M_4H_1)_{H_2O} + M_1H_1 = M_2H_2 + M_3H_3 + (M_4H_2)_{H_2O} \tag{3}$$

Thus, $M_4 = (0.087 \times 732) + (0.913 \times 108) - (1 \times -5)/(1150.4 - 168.0)$
$= 0.160$ lb steam/lb of strong solution entering the generator

Ammonia evaporated $= x_2M_2 = 0.945 \times 0.087 = 0.082$ lb/lb mixture circulated

The heat supplied by the steam is $0.160(1150.4 - 168.0) = 157.0$ Btu/lb of mixture circulated, or $157.0/0.087 = 1800$ Btu/lb of vapor leaving the generator.

EXERCISES

Properties of Mediums

1. Methane is diluted with carbon dioxide until the heating value of the mixture in Btu/ft^3 is 0.7 that of pure methane. Each gas is available at 15 lb/in.^{2} abs pr. The total pressure after mixing will be 14.85 lb/in.^{2} abs. Determine the desired volume and weight ratio of the gases as supplied and the partial pressure of each gas in the mixture. *Ans.* Vol. ratio = 0.429; wt. ratio = 1.179.

2. Air and CO_2 at a temperature of 150 F occupy a chamber having a volume of 14.4 ft^3. The total pressure of the mixture is 110 lb/in.^{2} abs, the air pressure being 10 lb/in.^{2} abs. Determine the volume and weight analysis of the mixture, (*a*) assuming perfect-gas relations, (*b*) using data from the Appendix for the CO_2.

3. Determine the amount of ammonia vapor to saturate 1 lb of air at 60 F. Total pressure is 200 lb/in.^{2} abs. *Ans.* 0.758 lb.

4. The volume analysis of air is 0.21 O_2, 0.78 N_2, and 0.01 A, approximately. Ten pounds of air at a pressure of 14.7 lb/in.^{2} abs are to be compressed to a pressure of 10,000 lb/in.^{2} and a temperature of 140 F. Determine the final volume, (*a*) assuming perfect-gas relations, (*b*) based on reduced conditions and compressibility factors.

5. Determine the amount of water vapor to saturate 1 lb of air at 60 F at sea level; also at the conditions at 50,000 ft altitude.

6. Determine the amount of water vapor per pound of air at a temperature of 0 F and a relative humidity of 60 per cent. Total pressure is 14.7 lb/in.^{2} *Ans.* 0.000471.

7. The mixture in Exercise 6 is heated at constant pressure to 70 F. Determine the relative humidity at this condition. *Ans.* 3.06 per cent.

8. A mixture of air and saturated water vapor is cooled from 140 to 0 F at a constant pressure of 14.7 lb/in.^{2} Determine the final volume, U and H per pound of air.

9. Compute and plot the specific and residual volumes of a mixture of methane and *n*-pentane, having a 0.3857 weight fraction of methane, at a temperature of 160 F and for various pressures in the various phases (see Fig. 55)

10. Evaluate and plot the residual volumes for a mixture of CH_4 and CO_2 having a 0.3583 weight fraction of CH_4 at the temperatures listed in Table XXIII, Appendix.

11. One pound of air at 60 F and at a pressure of 1 atm is mixed with 1 lb of CO_2 at the same conditions. The final temperature is 60 F and the total pressure is 1 atm. Determine the increase in entropy because of the mixing process. *Ans.* 0.0763 Btu/°R.

12. A chemically correct mixture of octane and air consists of $1\ C_8H_{18} + 12.5\ O_2 + 47\ N_2$. The products of reaction are $8\ CO_2 + 9\ H_2O + 47\ N_2$. Determine the entropy of a mixture of air and fuel, containing 0.9 lb of air, and of products resulting from 0.1 lb of air. The entropy of each of the constituents at 1 atm and 60 F is 0.

Processes

13. Determine the heat added for the process in Exercise 7.

14. A chamber contains 1 lb of air saturated with 1 lb of H_2O at 160 F. The chamber is cooled until the temperature is 0 F. Determine the heat removed from the mixture *Ans.* $Q = 1746$ Btu.

15. A mixture of CH_4 and CO_2 having a 0.3583 weight fraction of CH_4 is heated at a constant pressure of 3,000 lb/in.^{2} from 100 to 460 F. Determine the heat added per mole of mixture, assuming perfect-gas conditions.

16. One pound of H_2O is distributed in small liquid particles in 1 lb of air immediately before adiabatic isentropic compression in a compressor cylinder. The initial pressure and temperature are 14.7 lb/in.^{2} and 100 F, respectively. The mixture is compressed to 1/15 of the original volume. Determine the final pressure and temperature and the work per pound of air. Compare with the work of compressing the air alone. *Ans.* W = 184 Btu/lb of air alone; W = 112 Btu/lb of air; T_2 = 184 F.

17. A mixture containing a weight fraction of 0.3583 CH_4 in CO_2 at a pressure of 18 atm and a temperature of 100 F is compressed adiabatically and isentropically to 400 F. Determine the final pressure, the volumetric compression ratio, and the work requirement per mole of mixture, assuming perfect-gas conditions.

18. The atmospheric air is at 0 F and a relative humidity of 0.50. Determine the heat and H_2O requirements to change the condition of the air to 70 F and 70 per cent relative humidity. H_2O liquid is supplied at 50 F. Assume steady-flow conditions.
Ans. 28.6 Btu/lb of air.

19. It is proposed to condition the air in Exercise 18 by mixing the atmospheric air with steam under steady-flow conditions. Determine the required amount and condition of the steam. Steam pressure is 100 lb/in.^{2} abs.

20. Determine the volume of atmospheric air to be circulated per pound of liquid H_2O flowing to the cooling tower in the example, page 114, for air at leaving temperatures of 100, 110, 115, and 125 F. Plot the results against temperature.

21. A chamber contains 1 mole of air at 140 F and 14.7 lb/in.^{2} Sufficient liquid H_2O at 60 F is sprayed through a nozzle into the chamber to saturate the air. The pressure of the H_2O before being sprayed through the nozzle is 3,000 lb/in.^{2} Determine the equilibrium temperature of the mixture, assuming no heat transfer to or from the chamber.

22. The high-pressure vapor leaving the generator in the absorption refrigeration plant is condensed at a pressure of 140 lb/in.^{2} gage. The ammonia concentration of this vapor is 0.945 (see Example, page 116). This is the concentration also for the liquid after the condenser (Fig. 59). Determine the maximum temperature possible for the liquid and the heat removed from the condenser per pound of ammonia.
Ans. T = 84 F; Q_{out} = 655 Btu.

23. The liquid ammonia-water mixture flows through the expansion valve (Fig. 59) and has its pressure reduced from 140 to 20 lb/in.^{2} gage. The temperature ahead of the valve is 84 F. The ammonia concentration is the same as that of the liquid leaving the condenser in Exercise 22, or 0.945. Determine the liquid fraction of the fluids leaving the evaporator, if the temperature is maintained at 20 F, and the heat removed from the brine per pound of ammonia circulated.
Ans. Liquid fraction, 0.233; x_2 = 0.999; x_3= 0.753; Q_{in} = 392 Btu.

24. The condition of the strong liquid solution leaving the absorber is 20 lb/in.^{2} gage and 90 F. The condition of the weak solution entering the absorber is 20 lb/in.^{2} gage, and x_2 = 0.355 (see Example, page 116). The strong solution leaves the heat exchanger at 140 lb/in.^{2} and 100 F. Determine the temperature of the weak solution between the heat exchanger and the valve, assuming no heat loss from the heat exchanger.
Ans. 191 F.

25. Using the data given and obtained in Exercises 23 and 24, determine the heat removed from the absorber per pound of fluids entering from the evaporator.
Ans. 1555 Btu.

CHAPTER VII

AVAILABILITY OF ENERGY

Availability.—Energy is available in the thermodynamic sense when it can be converted completely into mechanical work. The availability of any form of energy is the measure of the *possibility of transforming that form of energy into mechanical work.* Although the Energy Equation for any given process accounts for all the forms of energy involved in the process, it does not indicate the maximum work obtainable from the form of energy supplied. The availability of the various forms of energy may be investigated by using two frictionless processes for each case:

1. Supply the form of energy to a medium in such a manner that all of the energy supplied appears in the same form in or associated with the medium.

2. Use a work process that transforms only the form of energy under consideration into work.

Potential energy of a given medium can be increased by raising it above the earth's surface. This may be accomplished by making use of the potential energy of another medium which descends sufficiently toward the earth's surface while exerting a force that elevates the original medium. In the ideal frictionless case, the decrease in potential energy of the one is equal to the increase in potential energy of the other.

The given medium can exert a force, equal to its weight, on a mechanism that moves and do work amounting to the decrease in potential energy while it is lowered to its original position. Consequently, potential energy is 100 per cent available in the ideal frictionless case.

Kinetic energy may be acquired by a medium by perfectly elastic impact with another medium possessing kinetic energy. The second medium may be considered a source of kinetic energy. The kinetic energy acquired by the first medium may be decreased by causing it to exert a force on a mechanism, which moves while gradually bringing the medium to rest, and thus kinetic energy is transformed into work. The evaluation of kinetic energy from the work obtainable (page 18) indicates that in the ideal frictionless case kinetic energy is 100 per cent available.

Flow work is evaluated also from the force-distance concept (Chap. II) and is therefore 100 per cent available in the ideal frictionless case, since the force can be applied to a moving mechanism as well as to a fluid. Thus, the steady-flow work evaluated for a medium entering a system containing an engine mechanism could be transformed wholly into mechanical work if fluid friction did not cause a pressure drop between the entrance of the system and the engine.

Internal energy of a medium, like potential energy, is measured above an arbitrary datum plane (see tables in Appendix). The internal energy of a medium can be increased by transferring internal energy from a hot medium to the given medium while held at constant volume. This is known as constant-volume heating, in which case

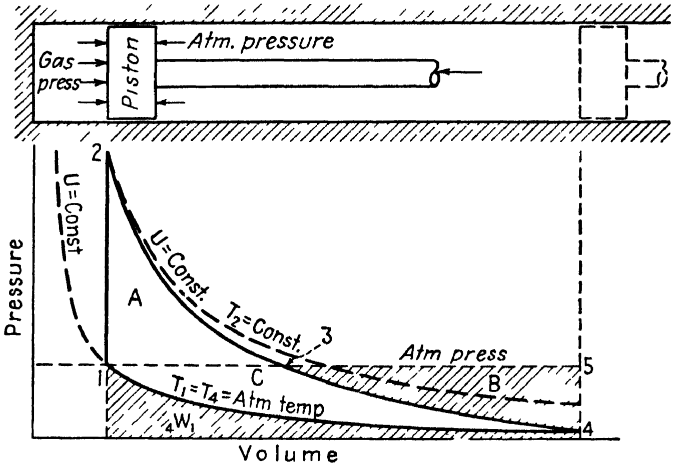

FIG 60.—Pressure-volume diagram for work values.

$$Q_{\text{in}} = U_2 - U_1 \tag{1}$$

Assuming the medium to be a perfect gas initially at atmospheric pressure and temperature (1, Fig. 60), this addition of internal energy will cause the pressure to be increased from 1 to 2. The medium is now in a condition to do work by exerting a force against an engine piston that may move. An ideal adiabatic expansion process transforms internal energy of the medium directly into work until the pressure of the medium is decreased to atmospheric at point 3, at which condition the pressure on both sides of the piston is atmospheric. For this process, the work done by the expanding gas on the piston is

$$W_{\text{out}} = U_2 - U_3 \tag{2}$$

Obviously, T_3 is higher than T_1 since V_3 is larger than V_1 for the same amount of medium at the same pressure. Thus, U_3 is greater than U_1, and

$$W_{\text{out}} < U_2 - U_1 \tag{3}$$

Thus, in a single process of adiabatic expansion of a medium against a piston mechanism, the atmospheric pressure limits the amount of internal energy originally supplied that can be converted into work. Actually, the net work out, considering the atmospheric pressure, is represented by the area 1-2-3 and is much less than $U_2 - U_1$, which is represented by the total area under the path 2 to 4 (Fig. 60).

Heat transferred to the medium results in the increase in internal energy in the foregoing case. Hence, the availability of the heat transferred is less than 100 per cent as already indicated for internal energy. Adding heat at constant pressure from 1 to 3 (Fig. 60) reduces the net work obtainable to zero. Thus the heat added at constant pressure is less available than that added at constant volume, indicating that the availability depends on the manner in which the heat is added. However, in this case the heat added is less than that added at constant volume.*

Chemical Energy.—No process is known whereby the chemical energy of a medium may be transferred as such to increase the chemical energy of another medium. Neither is a process known whereby chemical energy of a medium can be transformed directly into work.

The liberation of chemical energy by the combustion process at constant volume results in the transformation of chemical energy into internal energy of the products of reaction. This process places the same limitation on availability of chemical energy as on internal energy. However, when some mediums react, a large portion of the chemical energy is transformed directly into electrical energy which is 100 per cent available in the ideal case. Thus, for the electrochemical process such as occurs in the storage battery, the availability is very high as will be shown later.

Elimination of Atmospheric Pressure Limitation.—If the ideal adiabatic expansion process (Fig. 60) is continued until the temperature of the medium is reduced to T_4, which is atmospheric, the work on the piston amounts to $U_2 - U_1$, since $U_4 = U_1$ for a perfect gas. However, the net work because of the work of the piston on the atmosphere is represented by area A − area B. This is less than in the previous case where the process stopped with the medium at atmospheric pressure.†

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* This can be proved by comparing the Energy Equations for the two paths 1-2-3 and 1-3.

† Obviously, a double-acting cylinder might be used and the air might be removed so that a perfect vacuum could be assumed on the crank side of the piston. However, the minimum work required to remove the air would be equal to the work that the piston does on the atmosphere during the expansion stroke, and the net work would be the same as for this illustration.

The work done on the atmosphere during the expansion process can be regained if the piston is allowed to return to its original position. If the return stroke is an ideal adiabatic compression process, the medium will follow the path 4-3-2 and the net work of the series of processes will be zero. Thus, heat must be removed in order to reduce the work done on the medium during the return stroke, and the greater the amount of heat removed the lower will be the pressure and the smaller the work done on the medium during the return stroke. However, heat transfer necessitates a temperature difference (zero difference at the limit) between the medium in the cylinder and the medium to which the heat is rejected. Since the surrounding atmosphere is practically the lowest temperature medium available, the maximum work will be obtained with the isothermal compression process which returns the medium to its original condition at 1. Since the work done during compression, ${}_4W_1$, is represented by areas beneath the path 4 to 1,

$$\text{Net work (area } A + \text{area } C) = U_2 - U_1 - {}_4W_1$$

Thus, making use of the series of processes that returned the medium to its original condition (a cycle) eliminated the limitation imposed by the atmospheric pressure on the work obtainable from a given amount of internal energy or heat supplied. Although the net work is increased by the use of the cycle instead of the single process, the atmospheric temperature limits the possibility of transforming the internal energy or heat supplied into work. Thus, internal energy and heat are not 100 per cent available even with the cyclic process.

Carnot's Principle and Cycle.—The foregoing analysis for the availability of internal energy or heat supplied indicates the desirability of *heat rejection at the lowest possible temperature* from a medium undergoing a cyclic process. In 1824, Carnot recognized this criterion for maximum availability and also the desirability of *adding all of the heat* to a medium undergoing a cyclic process *at the highest possible temperature.* He also recognized the desirability of connecting these heat-addition and -rejection processes with adiabatic frictionless processes which do not result in any loss of availability. Thus, his cycle for maximum availability of heat supplied consists of the following four consecutive processes:

1. Addition of heat to the working medium at a constant temperature equal in the ideal case to the temperature of the hot body or *source* of heat.
2. Adiabatic expansion of the medium, without fluid friction, to the temperature of the cold body or *refrigerator*.
3. Rejection of heat from the medium at the constant temperature of the cold body or refrigerator.

4. Adiabatic compression of the medium, without fluid friction, to the initial condition.

This cycle results in the maximum amount of net work obtainable for the given temperature limits and is the criterion for availability in heat-engine processes. In any cycle (Chap. VIII) all energy terms that depend on the condition, position, or motion of the medium (point functions) are the same at the beginning and end of the cycle. Consequently, the Energy Equation for a cycle is

$$W_{in} + Q_{in} = W_{out} + Q_{out} \qquad (1)$$

Or, in an engine cycle,

$$\text{Net } W_{out} = W_{out} - W_{in}$$
$$= Q_{in} - Q_{out} \qquad (2)$$

The Carnot cycle is *rectangular* on the *T-S* diagram (Fig. 61). The area enclosed represents the difference between heat in and heat out, and this area is equivalent to the net work.

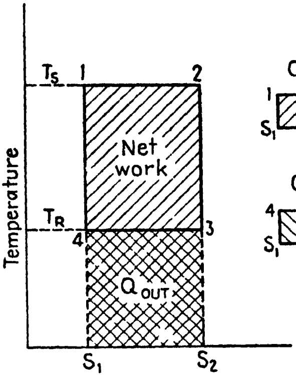

FIG 61 —*T-S* diagram of Carnot cycle.

The heat supplied to the medium at the source temperature T_S is

$$Q_{in} = T_S(S_2 - S_1) \qquad (3)$$

The heat rejected from the medium at the refrigerator temperature T_R is

$$Q_{out} = T_R(S_2 - S_1) \qquad (4)$$

and

$$\text{Net } W_{out} = (T_S - T_R)(S_2 - S_1) \qquad (5)$$

Also,

$$\text{Eff} = \frac{\text{Net } W_{out}}{Q_{in}} = \frac{T_S - T_R}{T_S} \qquad (6)$$

This represents the maximum efficiency possible for the heat-engine process, since the area of the ideal rectangular cycle on the *T-S* diagram is the largest work area for any assumed temperature and entropy limits, *i.e.*, for any given amount of heat supplied. The Carnot efficiency is independent of the medium since it depends only on source and refrigerator temperatures.

Example.—A Carnot cycle operates between a source temperature of 540 F and a refrigerator temperature of 140 F. Determine the efficiency of the cycle, the work out, the heat rejected to the refrigerator, and the entropy change during heat rejection per 1000 Btu of heat added.

$$\text{Eff} = \frac{T_S - T_R}{T_S} = \frac{1000 - 600}{1000} = 0.40$$
$$W_{\text{out}} = Q_{\text{in}} \times \text{eff} = 1000 \times 0.40 = 400 \text{ Btu}$$
$$Q_{\text{out}} = Q_{\text{in}} - W_{\text{out}} = 1000 - 400 = 600 \text{ Btu}$$
$$\Delta S = \frac{Q_{\text{out}}}{T_R} = \frac{600}{600} = 1.0 \text{ Btu/°R}$$

Unavailable Energy and Entropy.—The energy that cannot be transformed into work in the Carnot cycle is rejected as heat and is called *unavailable energy.* Thus, heat added to a medium may be divided into two parts as indicated by Carnot cycle analysis, namely, available (Q_A) and unavailable energy (Q_R), and,

$$Q_{\text{in}} = Q_A + Q_R \tag{1}$$

From Fig. 61,

$$Q_A/Q_{\text{in}} = (T_S - T_R)/T_S \tag{2}$$

and

$$Q_R/Q_{\text{in}} = T_R/T_S \tag{3}$$

or

$$Q_R = T_R(Q_{\text{in}}/T_S) = T_R\,\Delta S^* \tag{4}$$

and

$$\Delta S = Q_R/T_R \tag{5}$$

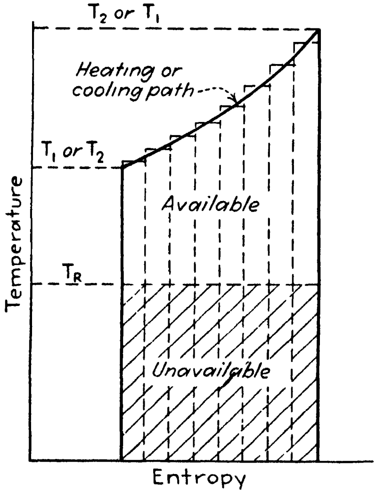

FIG. 62.—Application of Carnot cycle principle to process with changing temperature.

Thus, entropy is a measure of the unavailability of energy, an increase or decrease in entropy indicating an increase or decrease, respectively, of the unavailable energy transferred to or from a medium. Also, since T_R, the temperature at which heat is rejected, is constant in the Carnot cycle, unavailable energy change and entropy change are directly proportional to each other.

In general, the addition of heat to a medium increases both the available and the unavailable energy of the medium. The area on the T-S diagram representing the heat added is divided into these two parts by the refrigerator temperature, the area above being the available and that below the unavailable energy change. Likewise, the rejection of heat from a

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[*] This is apparent from Fig. 61, but it should be noted that the heat added or abstracted divided by the temperature at which the heat transfer occurs has already been defined as the change in entropy.

ΔS is the entropy change of either of the heat-transfer processes and not the entropy change for the cycle. Obviously this change is zero.

medium reduces both the available and the unavailable energy of the medium provided the temperature of the medium from which heat is rejected is above the refrigerator temperature.

For heat-transfer processes involving temperature change, the unavailable-energy change may be determined by assuming the heat to be supplied at various temperatures to a number of Carnot cycles adjacent to each other on the T-S diagram (Fig. 62). Each cycle receives a small amount of the heat at a temperature different from the other cycles, but the heat-input lines of the various cycles approach the path of changing temperature indicating the process as the number of cycles is increased to the limit.

Since T_1 is different for each cycle, Eq. (4) becomes

$$\text{Unavailable energy} = T_R\int_{T_1}^{T_2}\frac{Q}{T} = T_R\int_{T_1}^{T_2}\frac{Mc\,dT}{T} \tag{6}$$

which is the expression for unavailable energy change only for a medium that undergoes a temperature change during the heat-transfer process. It follows from Eq. (5) that for this process

$$\Delta S = \frac{Q_R}{T_R} = \int_{T_1}^{T}\frac{Mc\,dT}{T} \tag{7}$$

In using this relationship it should be noted that c is usually a function of T.

Example.—Determine the increase in available energy and entropy of 1 lb of H_2O when heated at a constant pressure of 14.7 lb/in.^{2} from 50 to 140 F. Assume a constant specific heat of 1.0 Btu/(lb × °F diff.). Refrigerator temperature is 50 F.

Since the temperature changes during the process,

$$Q_R = \int_{T_1}^{T_2} T_R Mc\frac{dT}{T} = T_R Mc \ln\frac{T_2}{T_1} = 510 \times 1 \times 1 \times \ln\frac{600}{510} = 82.92 \text{ Btu}$$

$$\Delta S = \frac{Q_R}{T_R} = \frac{82.92}{510} = 0.1626 \text{ Btu/°R}$$

From Table VI, Appendix, the entropy change along the saturated-liquid line, which is almost the same as for the constant-pressure path of 14.7 lb/in.^{2}, is found to be

$$[\Delta S]_{50^\circ}^{140^\circ} = 0.1984 - 0.0361 = 0.1623 \text{ Btu/°R}$$

The total heat supplied is

$$Q_{\text{in}} = \int Mc\,dT = Mc(T_2 - T_1) = 1 \times 1 \times (140 - 50) = 90 \text{ Btu}$$

Thus the increase in available energy is

$$90 - 82.9 = 7.1 \text{ Btu}$$

The determination of the change of entropy and unavailable energy for the constant temperature heat addition or rejection process has already been indicated in the treatment of the Carnot cycle. Thus

$$\Delta S = Q/T \tag{8}$$

and

$$Q_R = T_R \, \Delta S \tag{9}$$

The unavailable energy and entropy of a medium may be increased by a *self-acting process* occurring within the medium. In this case, provided the system is isolated, the increase in unavailable energy must equal the decrease in available energy because the total energy is constant. There are two processes that cause this so-called degradation of available energy to unavailable energy: the *heat-transfer* process and the *friction* process.

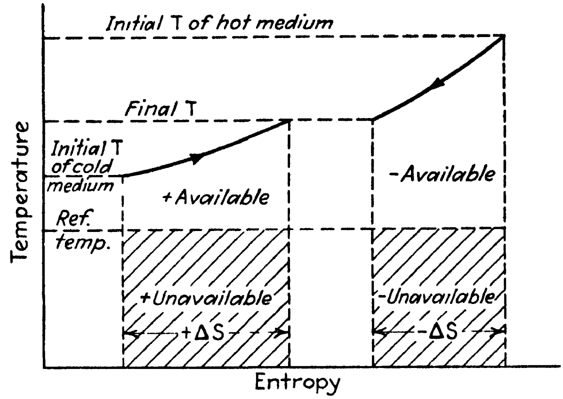

FIG. 63.—*T-S* diagram of heat-transfer process.

Heat-transfer Process.—Heat transfer occurs when a temperature difference exists between two mediums, or between two parts of the same medium. The heat is transferred by radiation, convection, and conduction. The transfer of heat usually causes the temperature of the hot medium to fall and that of the cold medium to rise, although heat transfer may occur at constant temperature. Since the heat rejected by the hot medium is equal to the heat absorbed by the cold medium, the areas beneath the paths representing the processes on the *T-S* diagram are equal in the ideal case. The area representing the heat rejected (Fig. 63) is higher and consequently has less width or change in entropy than the area representing the heat absorbed. Thus, the increase of unavailable energy and entropy of the cold medium is greater than the decrease of these items for the hot medium, while the decrease of available energy of the hot medium is greater than the increase for the cold medium. The same statements apply to heat transfer at constant temperatures for both mediums.

Example.—Two hundred pounds of H_2O at 25 lb/in.^{2} pr are divided into two equal parts having temperatures of 140 and 240 F. Determine the decrease in available energy caused by heat transfer that equalizes the temperature between the two parts. The refrigerator temperature is 40 F. Assume a constant specific heat of 1 Btu/(lb × °F diff.).

During temperature equalization the heat rejected by the hotter part is equal to the heat received by the colder part. Thus

$$Mc\ \Delta T_{\text{hot}} = Mc\ \Delta T_{\text{cold}}$$

Since the masses and specific heats are the same

$$T_{\text{hot}} - T_{\text{mix}} = T_{\text{mix}} - T_{\text{cold}}$$

or

$$T_{\text{mix}} = \frac{T_{\text{hot}} + T_{\text{cold}}}{2} = 650°\text{R}$$

The heat transferred is

$$Q_{\text{in}} = Q_{\text{out}} = 100 \times 1 \times (700 - 650) = 5000 \text{ Btu}$$

The unavailable energy change for the hotter medium is

$$T_R\ \Delta S = T_R \int_{T_1}^{T_2} Mc \frac{dT}{T} = 500 \times 100 \ln \frac{650}{700} = -3705 \text{ Btu}$$

The unavailable energy change for the colder medium is

$$T_R\ \Delta S = T_R \int_{T_1}^{T_2} Mc \frac{dT}{T} = 500 \times 100 \times 1 \ln \frac{650}{600} = 4000 \text{ Btu}$$

The energy and entropy values are summarized as follows:

Medium	Q	Q_R	Q_A	ΔS
Hot.	−5000	−3705	−1295	−7.41
Cold	+5000	+4000	+1000	+8.00
Mixture	0	+295	−295	+0.59

The net result is that no heat is added to or rejected from the mixture as a whole. However, the heat transfer between the two parts increased the unavailable energy of the mixture at the expense of the available energy of the constituents.

The net change of entropy for the 200 lb is

$$\Delta S = Q_r/T = 295/500 = 0.59 \text{ Btu/°R}$$

The foregoing example indicates that the entropy change in an isolated system is a direct measure of the change of unavailable energy.

Friction Process.—It has been shown that the atmospheric pressure limits the amount of internal energy originally supplied that can be transformed into work in a process. Also, the atmospheric or refrigerator temperature limits the amount of heat originally supplied that can be transformed into work in a cycle. However, it is always possible to transform work or any form of energy completely into internal energy or heat. A typical example is the transformation of the kinetic energy of a moving automobile into internal energy of the brakes when they are applied in stopping a car. The increase in internal energy of the brakes results in a temperature rise which causes heat transfer from them to the adjacent parts of the car and eventually to the surrounding atmosphere.

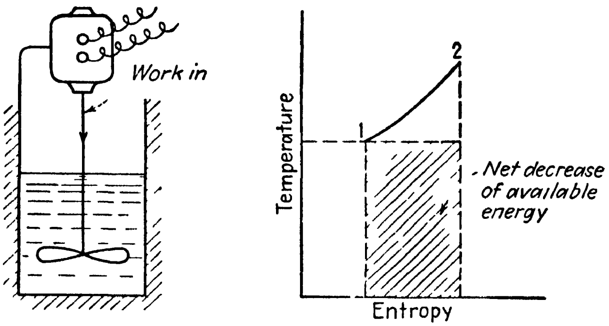

FIG. 64.—Dissipation of work by friction (available energy supplied).

The total amount of heat transferred from the brakes is equal to the work dissipated by friction at the brakes.

A paddle wheel immersed in water in a container (Fig. 64) may be driven by an electric motor, in which case, work is supplied to the paddle wheel and appears as an increase in energy of the water. The paddle wheel causes movement of the water and the various streams of water flowing at different velocities result in a shearing effect which dissipates the kinetic energy into internal energy.

If the water in the foregoing case is maintained at constant pressure the work done on the water will be

$$W_{\text{in}} = H_2 - H_1 \qquad (1)$$

The increase in enthalpy would be the same if the energy had been added by heat transfer from a hot body. Consequently, the area (Fig. 64) beneath the constant-pressure heating path on the T-S diagram represents the work done on the water. The area beneath the refrigerator temperature represents the increase of unavailable energy of the water as well as the decrease of available energy of the entire process, since all of the energy added was originally available.

The *T-S* diagram (Fig. 64) may also be used to represent the amount of kinetic energy dissipated by friction. In this case the area beneath the path represents $KE_1 - KE_2$, all of which was originally available. Thus, for a steady-flow process,

$$KE_1 + H_1 = KE_2 + H_2 \tag{2}$$

from which

$$KE_1 - KE_2 = H_2 - H_1 \tag{3}$$

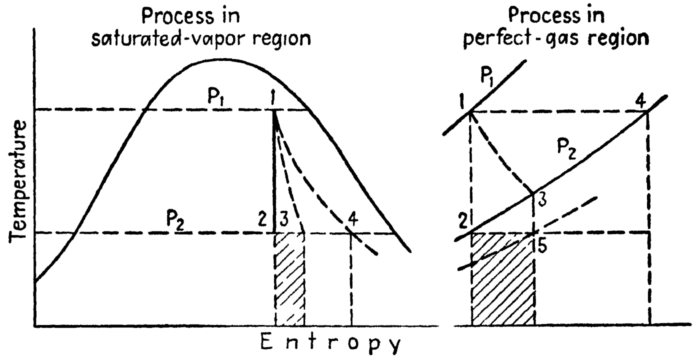
Process in saturated-vapor region
Process in perfect-gas region
Temperature
Entropy
P1
1
P2
2
3
4
P1
1
4
P2
3
2
5

FIG. 65.—Dissipation of kinetic energy by friction (self-acting process).

A steady-flow adiabatic constant-entropy process (Fig. 65) results in an appreciable increase in kinetic energy for an appreciable decrease in pressure. The Energy Equation for this process is

$$KE_1 + H_1 = KE_2 + H_2 \tag{4}$$

or

$$KE_2 - KE_1 = H_1 - H_2 \tag{5}$$

If some of the kinetic energy is dissipated by friction, H_2 will be increased to H_3 along the path 2 to 3.

Thus,

$$KE_3 - KE_1 = H_1 - H_3 \tag{6}$$

and the net energy dissipated by friction is

$$KE_2 - KE_3 = H_3 - H_2 \tag{7}$$

which is represented by the area beneath the refrigerator temperature between 2 and 3 if the process ends in the saturated region. This indicates the increase in unavailable energy because of the friction process. The friction may occur after point 2 has been reached or may occur while the expansion is taking place. The path for the first case is 1-2-3, while for the second case it is 1-3. In both cases the area beneath the path on the *T-S* diagram represents the total amount of kinetic energy that undergoes transformation during the friction process.

Assuming that the kinetic energy at point 1 (Fig. 65) is negligible and that all of the kinetic energy developed by each part of the pressure drop is immediately dissipated by the friction process, the constant-H line from 1 to 4 would represent the path of the process. The area under 2 to 4 is equal to $H_1 - H_2$ which is the maximum increase in kinetic energy possible by the given pressure or temperature drop, all of which has been made unavailable if the medium is in the saturated region. The area under the path 1 to 4 represents the total amount of kinetic energy that undergoes transformation during the friction process. This is greater in amount than the ideal increase in kinetic energy for the same pressure drop and is accounted for by the dissipation of kinetic energy into enthalpy at pressures above the lowest attained. This permits the enthalpy thus obtained to be partly converted again into kinetic energy by a further pressure drop, etc., until the final pressure is reached. Thus, the continuous dissipation of kinetic energy into enthalpy and its part regeneration into kinetic energy, etc., result in a total transformation of kinetic energy represented by the area under the path 1 to 3, which is larger than the ideal amount obtainable from the given pressure drop.

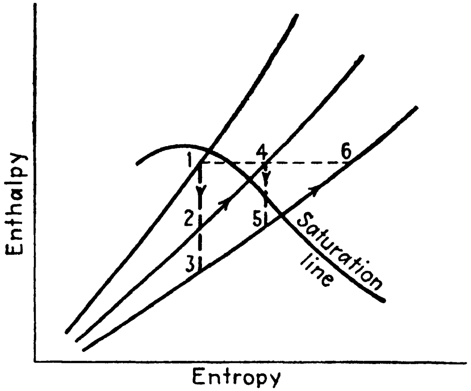

FIG. 66.—Effect of divergence of pressure lines on amount of KE undergoing friction process.

The foregoing can be seen on the Mollier diagram (Fig. 66) for a process having two ideal pressure drops with complete dissipation of the kinetic energy into enthalpy between the two parts and after the second part. The inherent divergence of the pressure lines on this diagram indicates that $H_4 - H_5$ is greater than $H_2 - H_3$ and therefore the total kinetic energy dissipated by friction from 2 to 4 and from 5 to 6 is greater than the kinetic energy obtained from the ideal process from 1 to 3. Obviously, replacing the two pressure drops by an infinite number of infinitely small pressure drops, with immediate dissipation of the resultant kinetic energy, is indicated by a path from 1 to 6 with the maximum amount of kinetic energy of the fluid dissipated by the friction process.

In the gaseous region (Fig. 65) the increase of unavailable energy accompanying similar friction processes is less than when the process is in the saturated region, since the dissipation of kinetic energy into enthalpy results in an increase in temperature of the gaseous medium. This increase in temperature indicates that some of the kinetic energy of the fluid that undergoes transformation during the friction process is again available at the end of the process. Thus, while $H_3 - H_2$ (Fig. 65) represents the kinetic energy transformed into enthalpy by the friction process for the path 1-2-3, the area 2-3-5 represents the part of this energy that is available at the end of the friction process for a gaseous medium. Also, the energy represented by the area under 2 to 3 ($H_3 - H_2$) is all unavailable if the medium is in the saturated region.

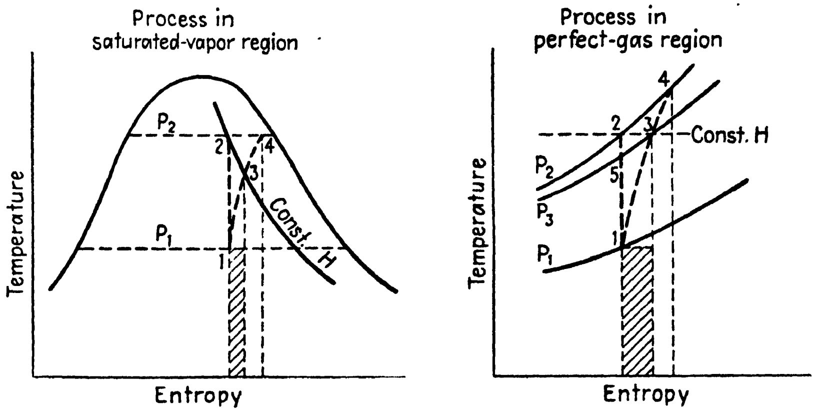

FIG. 67.—Effect of friction in adiabatic compression processes.

Decreasing the velocity of flow of a medium by a frictionless adiabatic process (the *diffuser* process) is represented by a constant-entropy line (1 to 2, Fig. 67). The Energy Equation for this process is

$$H_1 + KE_1 = H_2 + KE_2 \tag{8}$$

Fluid friction causes an increase in entropy, the resulting condition depending on the final kinetic energy and the amount dissipated by the friction process. The final enthalpy is determined from the Energy Equation

$$H_1 + KE_1 = H_3 + KE_3 \tag{9}$$

Equations (8) and (9) indicate that $H_3 = H_2$ if $KE_3 = KE_2$. For this case, points 2 and 3 are on the same H line. Again, the area beneath the path representing the process on the T-S diagram (1 to 3, Fig. 67) indicates the amount of kinetic energy that is transformed into enthalpy in the friction process.

Example.—H_2O at 14.7 lb/in.^{2} pr and at an entropy of 1.59 is flowing with a kinetic energy of 100 Btu/lb into a diffuser which reduces the kinetic energy to 20 Btu/lb. Fluid friction causes the entropy to increase 0.04 Btu/(°R × lb). Determine the approximate amount of kinetic energy dissipated by the friction process.

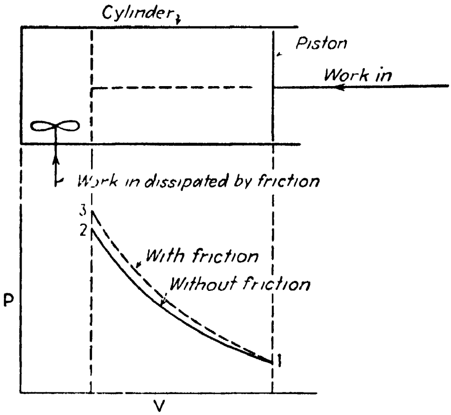

FIG. 68.—Effect of friction during compression on P-V diagram.

Substituting in the Energy Equation (Eq. 9) for this process,

$$1042 + 100 = H_3 + 20$$

$$H_3 = 1122 \text{ Btu/lb}$$

Also $$S_3 = S_1 + 0.04 = 1.59 + 0.04 = 1.63$$

At $H_3 = 1122$ and $S_3 = 1.63$, on the H-S diagram (Appendix), $P_3 = 33$ lb/in.^{2}, and $T_3 = 255$ F

The pressure that would have been attained in a frictionless process is indicated by the condition of $H_2 = 1122$ Btu/lb and $S_2 = 1.59$. These data indicate a pressure of 49 lb/in.^{2}

Assuming a straight line for the path of the friction process on the T-S diagram, the mean temperature for the process is $(212 + 255)/2 = 234$ F. The area beneath the path is equivalent to the kinetic energy which is transformed into enthalpy by the friction process. Thus,

$$T\,\Delta S = (234 + 460) \times 0.04 = 28 \text{ Btu}$$

Obviously, the highest final pressure is attained with the *self-acting compression process* if frictionless and if the final kinetic energy is zero.

The frictionless adiabatic compression process is represented by a constant-entropy line (1 to 2, Fig. 67). A rotary compressor imparts a velocity to the medium being compressed. This results in a fluid-friction effect which transforms some of the kinetic energy into internal energy and causes an increase in entropy during the compression process. This process is similar to that of stirring a medium being compressed in a cylinder (Fig. 68). In this case the work dissipated in the stirring process only is represented by the area beneath the path on the *T-S* diagram if the process is adiabatic. The area beneath the path on the *P-V* diagram is the work done by the piston on the medium being compressed. However, the total work required is the sum of the stirring and the piston work. The area under the path 1 to 3, or 1 to 4 (Fig. 67) represents the kinetic energy dissipated into internal energy in a nonflow process, or into enthalpy in a steady-flow process, of which only the portion above the refrigerator temperature is available at the end of the process. The area under 2 to 4 on the *T-S* diagram represents the increase in total work because of the friction process. Hence, the area 1-2-4-1 represents the additional work of compression (which can be shown on the *P-V* diagram) that is required because of the increase in enthalpy of the medium by the friction process.

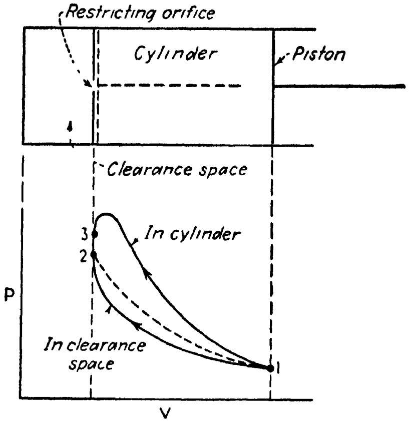

FIG. 69.—Friction process in compressor cylinder with restricting orifice.

The ratio between the increase in enthalpy for the adiabatic frictionless process (1 to 5, Fig. 67) to the increase in enthalpy for the actual process (1 to 3) is termed the *adiabatic efficiency* of the compressor or supercharger.

Ordinarily there is very little fluid friction during the compression of a medium in a compressor cylinder or during expansion of a medium in an engine cylinder. However, if the cylinder design is such that kinetic-energy or turbulent effects are introduced, fluid friction, entropy increase, and a loss of available energy will result. Any cylinder that has a throat or restricted passageway between the principal cylinder volume and the clearance space, as is the case for many internal-combustion engines, is the cause for such friction effects in the process occurring therein. The friction effects are negligible, however, if the piston is moved slowly. Assuming no heat transfer for such a compression process (the dashed line from 1 to 2, Fig. 69), the Energy Equation for the process is

$$U_1 + W_{\text{in}} = U_2 \tag{10}$$

or

$$W_{\text{in}} = U_2 - U_1 \tag{11}$$

If the piston is moved rapidly, a pressure difference will develop between the cylinder and the clearance space, and the pressure in the cylinder may be represented by the upper path, 1 to 3. In this case, if no heat transfer occurs

$$W_{\text{in}} = \int_1^3 P\,dV = E_3 - E_1 \tag{12}$$

where E_3 indicates the condition of all of the medium at equilibrium in the clearance space after all kinetic energy effects caused by the compression process have been dissipated. The pressure in the clearance space for the various positions of the piston is indicated by the lower path, 1 to 3. The increase in the entropy for this process may be determined from the initial and final conditions for the medium. It should be noted that the path for all the medium cannot be plotted on any diagram since the part in the cylinder proper and that in the clearance space are not at the same condition during the process. Thus, the two paths from 1 to 3 indicate only the pressure variation with the piston position.

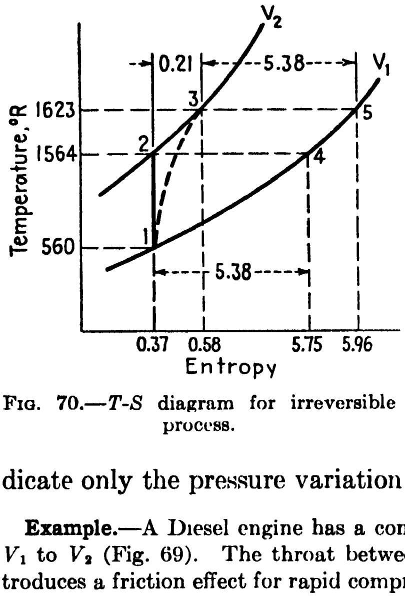

FIG. 70.—*T-S* diagram for irreversible process.

Example.—A Diesel engine has a compression ratio of 15 to 1. This is the ratio of V_1 to V_2 (Fig. 69). The throat between the cylinder and the clearance volumes introduces a friction effect for rapid compression which increases the work of compression to 10 per cent above that of the adiabatic isentropic process. Assume that the air at point 1 is at 14.7 lb/in.^{2} abs and at a temperature of 100 F. Determine the final temperature and pressure, and the entropy change of the air caused by the friction process.

Both the adiabatic isentropic process (1 to 2, Fig. 70) and the adiabatic friction process (1 to 3) start from the same initial condition and end at the same final volume. Assuming that the values of $\int c_v dT/T$ in Table XXI, Appendix, apply to the V_1 volume line,

$S_1 = 0.37$, and $S_4 - S_2 = R \ln (V_1/V_2) = 1.986 \ln 15 = 5.38$ Btu/(°R × mole)

From Table XXI, at $S_4 = 5.75 \quad T_4 = 1564°\text{R} = T_2$

Also from Table XIX,

$$\text{Ideal work} = U_2 - U_1 = 5515 - 196 = 5319 \text{ Btu/mole}$$

$$\text{Actual work} = 1.10 \times 5319 = 5851 \text{ Btu/mole}$$

From Table XIX, $T_3 = 1623°\text{R}$

Also, $P_3 = P_1V_1T_3/T_1V_2 = 14.7 \times 15 \times 1{,}623/560 = 639 \text{ lb/in.}^2$

From Table XXI at 1623°R, $S_5 = 5.96$ Btu/(°R × mole)

Also, $S_3 = S_5 - R \ln (V_1/V_2) = 5.96 - 5.38 = 0.58$ Btu/(°R × mole)

Hence, $S_3 - S_1 = 0.58 - 0.37 = 0.21$ Btu/(°R × mole)

An *unrestrained expansion process* is one in which pressure differences occur that produce kinetic energy effects which are dissipated by the friction process. A cylinder (Fig. 71) containing a medium at a pressure above atmospheric is opened to the atmosphere. Part of the medium escapes and pushes back the atmosphere while the pressure drops to atmospheric in the chamber. The Energy Equation for the process, assuming no heat transfer and that all the kinetic energy developed is dissipated by friction into internal energy of the medium, is

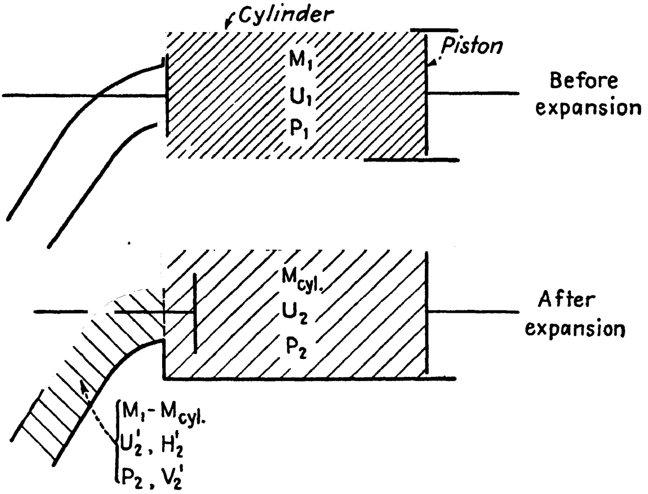

FIG. 71.—Unrestrained expansion process.

$$M_1U_1 = M_{cyl}U_2 + (M_1 - M_{cyl})(U_2' + P_2V_2') \tag{13}$$

$$= M_{cyl}U_2 + (M_1 - M_{cyl})H_2' \tag{14}$$

where the subscripts represent the conditions indicated in Fig. 71.

U_2 may be evaluated by assuming that the medium remaining in the cylinder undergoes a frictionless adiabatic expansion. This permits a solution for H_2' for the part that escapes from the cylinder. P_2 and H_2' indicate the entropy of the escaped part, and this in turn indicates the increase in entropy and the decrease in available energy resulting from the process.

Heat Transfer and Friction.—It has been shown that heat transfer into or out of a medium increases or decreases its entropy, respectively. The net entropy change for an isolated system consisting of a hot medium and a cold medium is always positive if the mediums involved are originally at different temperatures.

Also, it has been shown that the friction process always increases the entropy of the medium involved. A constant-entropy process may result if heat is withdrawn from a medium undergoing an internal friction process which exactly offsets the decrease in entropy caused by the heat transfer at each point along the path describing the process. Consequently, a constant-entropy process is not necessarily an adiabatic one. Also, when both heat transfer and friction occur, the entropy change of *all* the mediums involved in the heat transfer process must be considered.

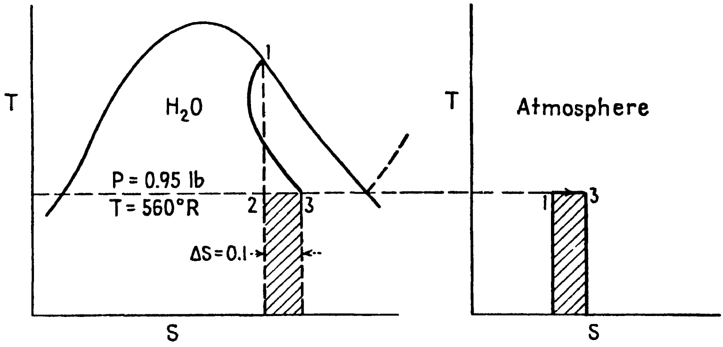

FIG. 72.—Restrained expansion process with heat transfer out and friction.

Example.—Steam flows through a turbine and 50 Btu of heat per pound of steam are transferred from the steam, through the turbine casing, and finally to the surrounding atmosphere. Also the steam undergoes a friction process in flowing through the nozzles and over the turbine blades. The net result of both the heat-transfer and the friction processes on the steam is an entropy increase of 0.1 Btu/(°R × lb). Determine the loss of available energy per pound of steam if the initial condition is 150 lb/in.^{2} abs and saturated, and the back pressure is 0.95 lb/in.^{2} abs.

The available energy for the ideal process (Fig. 72) is

$$H_1 - H_2 = 1194.1 - 873.9 = 320.2 \text{ Btu}$$

This represents the sum of the work done on the turbine rotor and the increase in kinetic energy of the medium, since the Energy Equation for the process is

$$H_1 + KE_1 = H_2 + KE_2 + W_{\text{out}} \tag{1}$$

For the actual process,

$$W_{\text{out}} + KE_3 - KE_1 = H_1 - H_3 - Q_{\text{out}} \tag{2}$$

Thus, the available energy obtained in the actual case is

$$1194.1 - 929.9 - 50 = 214.2 \text{ Btu/lb}$$

The refrigerator temperature in this case is 560°R. Hence,

$$\text{Net } \Delta S = (320.2 - 214.2)/560 = 0.1893 \text{ Btu/°R}$$

This should equal the sum of the entropy changes of the atmosphere receiving the heat and the steam that rejected the heat. Thus,

$$(50 \div 560) + 0.1 = 0.1893 \text{ Btu/°R}$$

100 F being used as the atmospheric temperature since the available energy of the steam in this problem is based on a refrigerator temperature of 100 F.

Entropy Equation.—The use of entropy as the abscissa of a temperature-entropy diagram was developed to permit the evaluation of heat added or abstracted by the area beneath the path representing the process. It has been shown that the area beneath the path describing the process on the T-S diagram is

$$\int T\,dS = Q_{\text{in}} - Q_{\text{out}} \tag{1}$$

only when the process is frictionless. Also, it has been shown that entropy of a medium always increases when it undergoes *only* a friction process. The area beneath the path representing the adiabatic friction process on the T-S diagram is equivalent to the total available energy, usually KE or W which undergoes transformation in the friction process. Therefore, in adiabatic friction processes,

$$\int T\,dS = (KE \text{ or } W)_F \tag{2}$$

In general then,

$$\int T\,dS = Q_{\text{in}} - Q_{\text{out}} + (KE \text{ or } W)_F \tag{3}$$

This is known as the Entropy Equation and is particularly useful for the analysis of processes for which a path can be drawn on the T-S diagram.*

In any cycle

$$Q_{\text{in}} - Q_{\text{out}} = W_{\text{out}} - W_{\text{in}} \tag{4}$$

Therefore,

$$W_{\text{out}} - W_{\text{in}} = \int T\,dS - (KE \text{ or } W)_F \tag{5}$$

If the path describing the cycle on a T-S diagram is followed in a clockwise direction, mathematical conventions indicate that $\int T\,dS$ will be positive, which is the case of the engine cycle. Equation (5) indicates that friction reduces the net work out of an engine cycle. If the cyclic path is followed in a counterclockwise direction, $\int T\,dS$ is negative and friction increases the net work done in a compressor cycle.

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* This implies that the medium is not undergoing any internal heat-transfer effects and is all at the same pressure at any point in the process. Obviously, Eq. (1) applied separately to the hot and cold parts of a medium may be used to evaluate the change in S for the internal heat-transfer process, but a path describing the process for the whole amount of the medium cannot be drawn.

The Carnot cycle (Fig. 73) has a work or available energy value equivalent to the area *ABCDA*. The introduction of a friction process *BE* increases the area enclosed by the cyclic path to *ABEDA* which is equivalent to $\int T\,dS$ taken around that cycle. The area representing friction effect is *BEFGB*. Thus $\int T\,dS - (KE \text{ or } W)_F$ is equal to area *ABEDA* − area *BEFGB*, or area *ABCDA* − area *CEFGC*. Thus, the available energy of the original Carnot cycle is decreased by the amount that the friction process increases the unavailable energy. This indicates that the path between *B* and *E* is of no particular consequence with regard to work evaluation, the important factor being that the entropy was increased from S_G to S_F during the friction process.

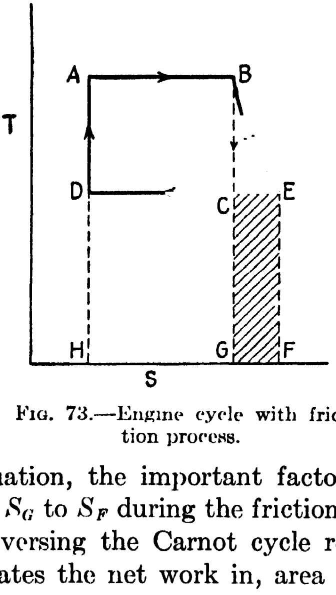

FIG. 73.—Engine cycle with friction process.

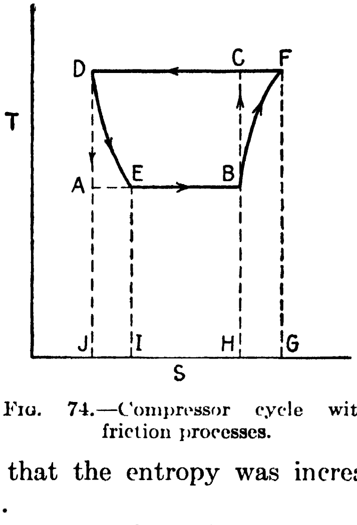

FIG. 74.—Compressor cycle with friction processes.

Reversing the Carnot cycle results in area *ABCDA* (Fig. 74), which indicates the net work in, area *ABHJA* indicates heat in, and the area *CDJHC* indicates heat out. Introducing a friction process for both the adiabatic compression and expansion processes results in cycle *DEBFD*, the area enclosed being the $\int T\,dS$ which will be negative in sign. The available energy $(KE \text{ or } W)_F$ which undergoes transformation during the friction process is represented by the areas under *DE* and *BF*, which, according to Eq. (5), added to $\int T\,dS$ results in area *JDFGHBEIJ*, which represents the net work in for the reversed cycle with friction.

In the foregoing, friction is shown to decrease the net work obtainable from an engine cycle and to increase the net work required in the reversed or compressor cycle. In both cases the paths indicating the friction processes are of no particular consequence in evaluating the net work of the cycle if the end points of the friction processes are known. In some cases the path for the friction process cannot be drawn since the medium may not be in equilibrium during the friction process. Also, in a cycle the net work effect can be obtained always from the algebraic summation of the heat-transfer effects [see Eq. (4)].

Reversibility and Irreversibility.—A process is reversible if, when reversed in direction, all parts of the process occur in the reversed order and all mediums involved are returned to the original conditions existing before the process occurred. This indicates that the availability of energy before and after a reversible process is the same.

It has been shown that the heat-transfer process with finite temperature difference results in a loss of availability. It is therefore an irreversible process. However, if the hot body is at the same temperature as the cold body (ΔT approaching zero as the limit), there will be no loss of availability and consequently the heat-transfer process approaches reversibility as the temperature difference between the two bodies approaches zero. The heat-transfer processes of the Carnot cycle are assumed to be reversible, indicating that the source of heat supply is at the same temperature as the medium receiving the heat; also, that the medium is at the refrigerator temperature when rejecting heat. Actually, all processes require finite temperature differences to obtain appreciable heat transfer in a reasonable time and are consequently irreversible.

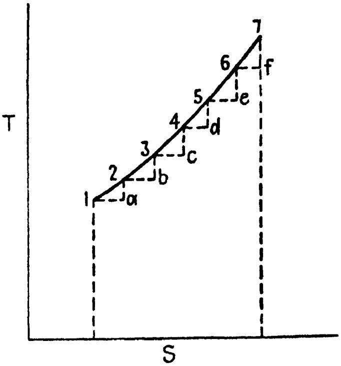

Fig 75.—Reversible heat-transfer process with temperature change.

The adiabatic expansion or compression of a medium in an engine or compressor cylinder is reversible if no fluid friction effects are developed in the medium during expansion or compression. The adiabatic condition is approached in practice if the process occurs rapidly. However, this tends to introduce the kinetic energy effects that make the process irreversible. Thus, in practice, there are no reversible processes either because of heat-transfer or friction effects, but reversibility is approached as a limiting condition.

A process that results in a change of temperature with heat transfer to or from a medium may approach reversibility if an infinite number of heat sources or refrigerators at various temperatures throughout the temperature range of the process are provided. Assume that a number of heat sources at temperatures T_1, T_2, etc. (Fig. 75), are available. A small amount of heat may be drawn from the source at T_1 and added to the medium at T_1, indicated by the path 1 to a. At a the medium is compressed adiabatically and reversibly to point 2. Then heat is transferred from the source at T_2, etc., point 7 finally being attained by the series of reversible processes. Obviously, as the number of sources approaches infinity, the broken path approaches the actual path and the process can be said to approach reversibility in the limit.

The Carnot cycle is an ideal cycle consisting of four reversible processes which can be approached but never attained. Consequently, this cycle is considered the limiting case. Any cycle may be *reversed* or run in the opposite direction, but only the Carnot cycle is *reversible*, which indicates that the work obtained from the engine cycle for a given temperature difference is that required to operate the cycle when reversed.

If it be assumed that an engine is more efficient than the Carnot engine, it would be possible to have this engine drive a Carnot engine reversed and result in a net transfer of heat from the refrigerator at low temperature to the source at high temperature. This transfer of heat from a low temperature to a high temperature by a self-acting process is contrary to all experience and is consequently considered impossible. Thus, the conclusion is reached that no engine can be more efficient than a reversible one.

Second Law of Thermodynamics.—The principle of the Second Law of Thermodynamics is that of the *degradation of energy* from the available to the unavailable condition. The potential energy of a body of water above sea level is theoretically all available energy. If the water is allowed to flow naturally to the sea, the available potential energy is dissipated. Internal energy in a medium at high temperature has a definite availability if used immediately in a heat-engine process. However, if not used immediately, temperature difference between the medium and the surroundings causes heat transfer and temperature drop of the medium that reduces the availability of the internal energy to zero when the medium is cooled to atmospheric temperature.

Both mechanical and fluid friction, which are always present, reduce the availability of energy.

Since all processes observed have shown this inherent degradation of available to unavailable energy, and only hypothetical reversible processes have been conceived which do not change the availability, and no process has been observed or conceived that could increase the availability of energy in an isolated system, the principle of the degradation of energy has been universally accepted.

Clausius was the first to state the Second Law. This he did in the form

$$\Sigma(Q/T) \geqq 0$$

which is proved in the heat-transfer process, p. 126. He also stated, *It is impossible* *for a self-acting machine unaided by any external agency to convey heat from one body to another at higher temperature.*

Kelvin stated, *It is impossible by means of inanimate material agency to derive mechanical effect from any portion of matter by cooling it below the temperature of surrounding objects.*

Planck* stated, *It is impossible to construct an engine which will work in a complete cycle and produce no effect except the raising of a weight and the cooling of a heat reservoir.*

A machine that will produce a work effect greater than the energy supplied is a *perpetual-motion machine of the first class* and violates the First Law of Thermodynamics.

A machine that will operate without a source of energy, although producing no work effect, is a *perpetual-motion machine of the second class* and violates the Second Law of Thermodynamics (Ostwald).

Thermodynamic- and Gas-temperature Scales.—An absolute-zero temperature and thermodynamic-temperature scale based upon the Carnot cycle were first proposed by Lord Kelvin. Absolute zero is the temperature which, when used as the temperature of the refrigerator for the Carnot cycle, results in an efficiency of 100 per cent for the cycle. A temperature lower than absolute zero for the refrigerator temperature would indicate a Carnot-cycle efficiency greater than 100 per cent. Thus, more work would be obtained than heat input and this would violate the Principle of Conservation of Energy.

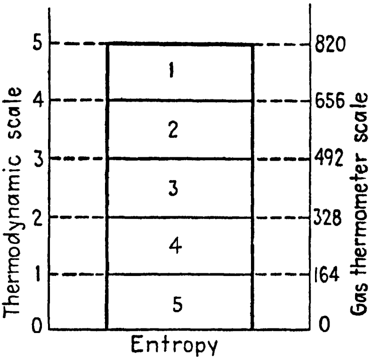

FIG. 76.—Thermodynamic- and gas-thermometer scales.

The thermodynamic scale may be established from a series of Carnot cycles located between any temperature and the thermodynamic zero, each cycle having the same work area, and the refrigerator temperature of the first being the source temperature for the second cycle, etc.

In Fig. 76, five such cycles have been inserted between a given temperature, 5, and the absolute zero, for the purposes of illustration. Each cycle has a work area equivalent to one-fifth of the heat input to the first cycle. Therefore, an arbitrary scale of 5 and 4 can be used for the source and refrigerator temperatures, respectively, for the first cycle, etc. Thus, a thermodynamic-temperature scale ranging from 0 to 5 by equal increments is established for this illustration. This scale is unique in that it is independent of the medium and of the upper temperature.

The gas-thermometer scale is based upon the decrease in pressure of a constant volume of a so-called *perfect* gas as the temperature is reduced. This indicates an absolute zero of 491.7 F below the freezing temperature for water under a pressure of 14.7 lb/in.^{2} abs, at which temperature the pressure and internal energy of the gas as herein defined would be zero. Thus, it would be impossible to expand such a gas if used in a Carnot cycle to a lower pressure or temperature, for all of the internal energy of the gas would have been transformed into work when the absolute zero on the gas-thermometer scale was reached. This would leave no internal energy in the gas to be rejected to a refrigerator at absolute zero temperature, indicating the maximum efficiency of 100 per cent.

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*PLANCK, Max, "Treatise on Thermodynamics," p. 89, 3d Eng. ed., trans. from 7th German ed. by A. Ogg, Dover Publications, 1945.

Since in each case the efficiency of a Carnot cycle is 100 per cent when each absolute-zero temperature is used for the refrigerator, it is obvious that the absolute zeros are identical and it merely requires correlation at some other temperature to fix the relation between the scales. Thus, if the refrigerator for the second Carnot cycle (Fig. 76) is at the freezing point of water, the gas-thermometer scale is related to the thermodynamic scale as shown. Since the two scales are directly proportional to each other, the thermodynamic scale can be made the same as the gas-thermometer scale.

Availability of Chemical Energy.—The source of energy for the heat-engine or internal-combustion engine process is the chemical energy liberated by the combustion process. The liberation of chemical energy in this manner results in products of reaction at a high temperature. This is an irreversible process and consequently results in an increase in entropy and a loss of availability of the energy involved.

Some chemical reactions, such as occurring in the battery process, result in the transformation of chemical energy directly into electrical energy without appreciable temperature rise of the constituents. Except for the slight heating effect, this process is reversible and consequently the chemical energy liberated in this process has a very high availability, since electrical energy is almost 100 per cent available.

The Energy Equation for the constant-temperature chemical-electrical process at constant pressure or for steady-flow conditions is

$$C_{\text{react}} + H_{\text{mix}} + Q_{\text{in}} = H_{\text{prod}} + Q_{\text{out}} + EE_{\text{out}} \qquad (1)^*$$

or

$$EE_{\text{out}} = C_{\text{react}} + (H_{\text{mix}} - H_{\text{prod}})_T + (Q_{\text{in}} - Q_{\text{out}}) \qquad (2)$$

Also,

$$Q_{\text{in}} - Q_{\text{out}} = T(S_{\text{prod}} - S_{\text{mix}})_T$$

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[*] Only one of the Q values will be required depending on the mediums undergoing reaction.

The availability of the chemical energy is the ratio of the electrical energy obtained to the *heat of reaction*. And,

$$Q_{\text{react}} = C_{\text{react}} + (H_{\text{mix}} - H_{\text{prod}})_T \qquad (3)^*$$

Example.—Assume that a method has been developed for obtaining electrical energy directly from the reaction

$$CO + 0.5O_2 = CO_2$$

The CO and $0.5O_2$ are mixed before entering the reaction chamber and are at a total pressure of 14.7 lb/in.^{2} abs and a temperature of 140 F. A constant-temperature process is maintained and the CO_2 leaves the reaction chamber at 14.7 lb/in.^{2} abs pr. Determine the efficiency of the process.

The chemical energy for this reaction is 121,181 Btu/mole of CO (Table XXIV).

$$H_{CO} + 0.5H_{O_2} = 396 + 201 + 1.5 \times 1192 = 2385 \text{ Btu (Table XIX)}$$

Also, $H_{CO_2} = 570 + 1192 = 1762$ Btu (Table XIX)

Thus, $H_{\text{mix}} - H_{\text{prod}} = 2385 - 1762 = 623$ Btu

The entropy change for this reaction at 520°R is 20.71 Btu/°R (Table XXV). This is based on the entropy of all constituents being at a pressure of 1 atm. The entropy increase because of the irreversible mixing of 1 mole of CO and 0.5 mole of O_2 is

$$\Delta S_{\text{mix}} = R \ln 1.5 + 0.5 R \ln 3 = 1.90 \text{ Btu/°R}$$

Also, from Table XXII, at 1 atm and 140 F

$$\Delta S = S_{\text{mix}} - S_{\text{prod}} = 0.28 \text{ Btu/°R}$$

Thus, $Q_{\text{out}} = T(S_{\text{react at 520}} + \Delta S_{\text{mix}} + \Delta S) = 600(20.71 + 1.90 + 0.28) = 13{,}734$ Btu

Then, $EE_{\text{out}} = 121{,}181 + 623 - 13{,}734 = 108{,}070$

Substituting the proper values for the given reaction into Eq. (3) results in

$$Q_{\text{react}} = 121{,}181 + 623 = 121{,}804$$

Then,

$$\text{Eff} = \frac{108{,}070}{121{,}804} = 0.89$$

Entropy a Point Function.—Pressure, volume, and temperature indicate the state of a given amount of medium. Internal energy and enthalpy of a medium are point functions and consequently depend on the state of the medium and not on the processes that resulted in the state under consideration. However, work and heat transfer depend on the process and therefore are not point functions.

Entropy change of a medium was originally defined as the heat transferred (*not a point function*) divided by the absolute temperature (*a coordinate*) of the medium undergoing the process. It has also been shown that entropy change is equal to the available energy (kinetic energy or work) which undergoes the friction process divided by the absolute temperature of the medium in which the process occurs. In order to use entropy as a coordinate for a diagram describing the properties of a medium, it is necessary to prove that entropy is a point function.

Paths for reversible adiabatic expansion or compression processes can be drawn on a P-V diagram. These are lines of constant entropy (S_1 and

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* See the chapter on The Combustion Process.

S_2, Fig. 77) and may be assigned values by arbitrarily fixing the value for one line and determining the entropy of the others by intersecting all such lines with a constant-pressure line. The Energy Equation for the constant-pressure process from 2 to 1 (Fig. 77) is

$$U_2 + {}_2Q_1 = U_1 + {}_2W_1 \tag{1}$$

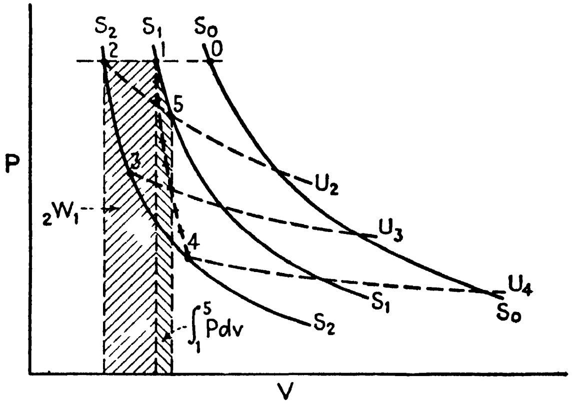

FIG. 77.—Sketch of constant U and S lines on P-V diagram.

The work value can be obtained from the area beneath the path on the P-V diagram, and values of U_2 and U_1 from the coordinates P and V, or from the values of the constant-U lines drawn through the various points. Thus ${}_2Q_1$ can be evaluated, and

$$S_1 - S_2 = \Sigma \frac{Q}{T} \tag{2}$$

the summation being taken over all increments of Q between states 2 and 1. Adding this entropy change to S_2 results in S_1, the entropy value assigned to the reversible adiabatic through point 1.

The path of each constant-entropy line is determined from the relation between internal energy and work for the reversible-adiabatic process. For the S_1 line,

$$U_1 = U_5 + {}_1W_5 = U_2 + {}_1W_5 \tag{3}$$

Consequently, point 5 is determined by locating the S_1 line so that

$$U_1 - U_2 = \int_{V_1}^{V_5} P\,dV \tag{4}$$

and other points in between are located in a similar manner. Thus the constant-S lines will intersect the constant-U lines.

The constant-U lines do not intersect each other since internal energy is a point function and consequently two values of U cannot be assigned to a given point. Thus, it must be proved that the constant-S lines do not intersect. Hence, assume that the S_1 line passes through points 1 and 4 intersecting S_2 at point 4. For the constant-pressure process from 2 to 1 it has been shown that heat is added and consequently S_1 is greater than S_2. Applying the Energy Equation to the path between point 4 on the S_2 line and point 4 on the assumed S_1 line results in

$$(U_4)_{S_2} + {}_4Q_4 = (U_4)_{S_1} + {}_4W_4 \tag{5}$$

Obviously, ${}_4W_4$ is zero, and ${}_4Q_4$ is zero since there can be only one value for U at point 4. Thus, since no heat is abstracted, there can be no change in S for a reversible process, proving that the S lines do not intersect.

Assume that at point 4 the entropy is increased from S_2 to S_1 because of the dissipation of kinetic energy by friction. The Energy Equation for the process is

$$(U_4)_{S_2} + KE = (U_4)_{S_1} \tag{6}$$

Obviously, U_4 on the assumed S_1 line cannot be greater than U_4 at S_2 since U is a point function. Hence, there can be no kinetic energy dissipated by a friction process in this case, and the medium at point 4 can have only one entropy value. Since it has been shown that the constant-entropy lines do not intersect on the P-V diagram, the conclusion may be drawn that each point has a unique entropy value, and therefore entropy is a point function.

EXERCISES

1. Assume that 1 lb of air at atmospheric conditions of 14.7 lb/in.^{2} and 60 F is in a piston-cylinder mechanism (see Fig. 60). Heat is added at constant volume until the temperature of the medium is 1500°R.

a. Determine the various volumes and the gross and net work obtained if the medium expands reversibly and adiabatically (1) to atmospheric pressure (2) to atmospheric temperature.

b. Determine the net work of the cycle 12341, Fig. 60.

c. Determine the efficiency of the cycle and compare with the Carnot efficiency for the same temperature limits.

Ans. *a*(1). 27.2 Btu; *a*(2). −360 Btu; *b*. 78.6 Btu; *c*. 0.44 and 0.65.

2. One pound of H_2O is heated at a constant pressure of 20 lb/in.^{2} from 60 to 500 F. Determine the increase of available and unavailable energy. Refrigerator temperature is 60 F. *Ans.* Q_A = 303.6 Btu; Q_R = 954.9 Btu.

3. One mole of N_2 is cooled at constant volume from a temperature of 1540 to 140 F. Determine the decrease of available and unavailable energy. Refrigerator temperature is 60 F. *Ans.* Q_A = 4264 Btu; Q_R = 3330 Btu.

4. Check the heat-transfer example on page 127, using data from the saturated table for H_2O.

5. Ten pounds of H_2O at a pressure of 50 lb/in.^{2} abs and a temperature of 500 F, are cooled at constant pressure to 100 F while transferring heat to a quantity of H_2O

at a constant pressure of 14.7 lb/in.^{2} abs. The temperature of the colder medium increases from 0 to 100 F during the process. Determine the net change of available energy and entropy for the process. Refrigerator temperature is 0 F.

Ans. Net $Q_A = -3447$ Btu; Net $\Delta S = 6.63$ Btu/°R.

6. A steam boiler contains 10,000 lb of saturated liquid H_2O and 100 lb of saturated H_2O vapor at a pressure of 200 lb/in.^{2} abs. The boiler is standing in the atmosphere, the fire is dumped, and eventually heat transfer to the atmosphere cools the H_2O to 60 F, the temperature of the atmosphere. Determine the net change of entropy for the process. *Ans.* Net $\Delta S = 1461$ Btu/°R.

7. A paddle wheel immersed in 1 lb of H_2O at 60 F absorbs 100 Btu of work while stirring the H_2O. Assuming that the process is adiabatic, determine the net change in available and unavailable energy, and in entropy. The H_2O is initially at 60 F and is stirred at a constant pressure of 14.7 lb/in.^{2} abs.

8. Solve Exercise 7 using 1500 instead of 100 Btu of work.

9. Saturated H_2O vapor at 150 lb/in.^{2} abs expands adiabatically to a pressure of 14.7 lb/in.^{2} abs in an engine cylinder. A restriction in the cylinder decreases the work of the steam on the piston to 90 per cent of the amount obtainable in the ideal process. Determine the entropy increase of the steam and the increase in unavailable energy, after equilibrium has been attained in the cylinder. Refrigerator temperature is 60 F.

10. H_2O at a pressure of 200 lb/in.^{2} abs and a quality of 0.90 enters a nozzle with a negligible velocity. The discharge pressure of the nozzle is 14.7 lb/in.^{2} abs. Fluid friction during flow through the nozzle results in an increase of entropy of 0.05 Btu/(lb × °R). Determine the loss of kinetic and available energy. Refrigerator temperature is 60 F. *Ans.* 33.5 Btu; 26 Btu.

11. Solve Exercise 10 assuming the initial pressure is 50 lb/in.^{2} abs and the initial temperature is 400 F. *Ans.* 34.5 Btu; 26 Btu.

12. Estimate the total amount of kinetic energy which undergoes transformation during the friction process if the process is adiabatic and the path is one of constant enthalpy. The initial conditions are the same as in Exercise 10. Also what percentage of the ideal kinetic energy is this total kinetic energy? *Ans.* 112 per cent.

13. Determine the ideal stagnation or ram pressure and temperature attainable in an air-intake system on a plane traveling at various speeds from 100 to 1,000 mph at various altitudes. See Table III, Appendix, for standard air conditions at various altitudes.

14. Air enters a supercharger at an atmospheric pressure of 14.7 lb/in.^{2} abs and a temperature of 60 F. The adiabatic efficiency is 0.75.

a. Determine the power required to compress 1 lb of air per sec to 2, 3, and 4 atm.

b. Determine the increase of unavailable energy, assuming that the refrigerator temperature is 60 F.

c. Determine the available energy undergoing the friction process, assuming that the path is a straight line on the *T-S* diagram (see Fig. 67).

d. Compare the result for *c* with the additional work required because of friction.

15. Saturated H_2O vapor at a pressure of 150 lb/in.^{2} abs enters a turbine and expands isentropically to a pressure of 0.95 lb/in.^{2} abs. During the process 50 Btu of heat per lb of medium are transferred out of the steam. Determine the loss of available energy. Is this equal to the net increase in unavailable energy? Atmospheric temperature is 100 F.

16. How much kinetic energy undergoes transformation during the friction process in Exercise 15? Give proof.

$$Q_{out} = H_D - H_E = 842.7 - 69.1 = 772.6 \text{ Btu}$$
$$W_{out} = Q_{in} - Q_{out} = 1677.2 - 772.6 = 904.6 \text{ Btu}$$
$$\text{Cycle eff} = \frac{W_{out}}{Q_{in}} = \frac{904.6}{1677.2} = 0.539$$

Checking the work values from the steady-flow analysis of the work processes,

$$\text{Hg turbine work} = M(H_{C'} - H_{D'}) = 12.47(149.7 - 106.1) = 543.7 \text{ Btu}$$
$$H_2O \text{ turbine work} = (H_C - H_D) = 1202.8 - 842.7 = 360.1 \text{ Btu}$$
$$\text{Gross work} = 903\ 8 \text{ Btu}$$

This checks the first solution for work out in which the pump work also was neglected.

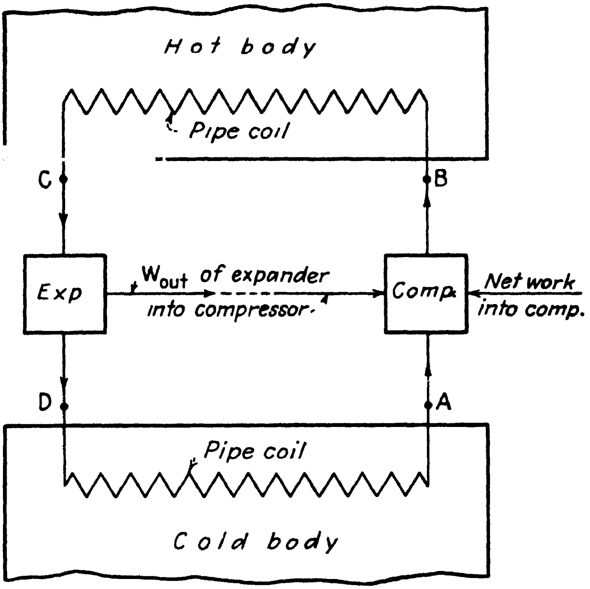

FIG. 91.—Flow diagram for gas refrigeration or heating cycle.

Gas Refrigeration or Heating Cycle.—The medium in this cycle remains in the gaseous state in all the processes. The medium at cold-body temperature in the ideal case (*A*, Figs. 91 and 92) is compressed adiabatically and reversibly to some temperature, *B*, above that of the hot body. Heat is rejected as the medium cools at constant pressure from *B* to *C*, decreasing in temperature to that of the hot body in the ideal case. The medium at *C* is expanded adiabatically and reversibly to *D*, which is at the same pressure as *A*. The medium then absorbs heat at constant pressure from *D* to *A* from the cold body, rising in temperature to that of the cold body in the ideal case.

The medium from *D* to *A* is a refrigerant, while from *B* to *C* it is a source for heat. Work is required from *A* to *B* and work is obtained from

C to D. On the P-V diagram (Fig. 92) the work required by the compressor is equivalent to the area $ABFE$, while the work obtained from the expander is represented by the area $CDEF$.

In any cycle,

$$W_{\text{in}} - W_{\text{out}} = Q_{\text{out}} - Q_{\text{in}} \tag{1}$$

Since the heating and cooling processes occur at constant pressure,

$$W_{\text{in}} - W_{\text{out}} = (H_B - H_C) - (H_A - H_D) \tag{2}$$

$$= (H_B - H_A) - (H_C - H_D) \tag{3}$$

in which case the first term represents the compressor work and the second term the expander or engine work.

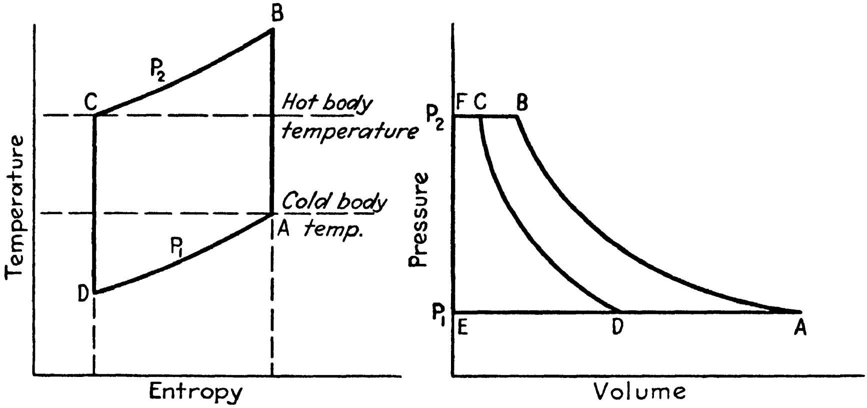

FIG. 92.—T-S and P-V diagrams of ideal gas-refrigeration and heating cycle.

Example.—Air is used in a gas refrigerating and heating cycle which operates between 1 and 10 atm pr. The cold body is at 0 F, while the hot body is at 70 F. Determine the heat removed from the cold body, the heat rejected to the hot body, the net work required, and the coefficient of performance, both as a refrigerating and as a heating cycle.

From Table XXII, Appendix, at 0 F the $\int c_p dT/T$ per mole of air is -0.84. At the end of adiabatic reversible compression the temperature, T_B, will be indicated by a value of $\int c_p dT/T$ of $-0.84 + 1.986 \ln 10$, or 3.73. Interpolating for this value in Table XXII indicates a value of 883°R for T_B.

Also, $$T_D = T_C T_A / T_B = 530 \times 460/883 = 276\text{°R*}$$

From Table XIX, $$Q_{\text{out}} = H_B - H_C = (1828 + 1753) - (48 + 1052)$$
$$= 2481 \text{ Btu/mole of air}$$

Also, $$Q_{\text{in}} = H_A - H_D = c_p(T_A - T_D)$$
$$= 6.84\ (460 - 276) = 1259 \text{ Btu/mole}$$

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* This is an approximation since the relation used is correct only for a medium having constant specific heats.

Then, Net work $= Q_{\text{out}} - Q_{\text{in}} = 2481 - 1259 = 1222$ Btu/mole

$$\text{Refrigerating coefficient of performance} = \frac{Q_{\text{in}}}{\text{net work}} = \frac{1259}{1222} = 1.03$$

$$\text{Heating coefficient of performance} = \frac{Q_{\text{out}}}{\text{net work}} = \frac{2481}{1222} = 2.03$$

The coefficients for the reversed Carnot cycle for the same hot- and cold-body temperatures would be as follows:

$$\text{Refrigerating coefficient of performance} = \frac{T_1}{T_1 - T_2} = \frac{460}{70} = 6.57$$

$$\text{Heating coefficient of performance} = \frac{T_2}{T_1 - T_2} = \frac{530}{70} = 7.57$$

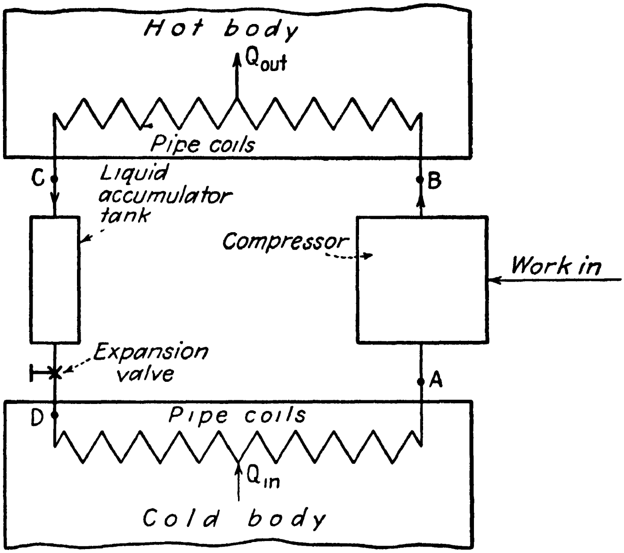

FIG. 93.—Flow diagram for vapor-compression refrigeration or heating cycle.

The gas-cycle performance coefficients are much lower than those of the Carnot cycle. However, the use of a lower pressure ratio will increase the performance coefficients of the gas cycle but will reduce the heat-transfer values per mole of air circulated.

Vapor Refrigeration or Heating Cycle.—In the ideal vapor cycle, either slightly wet, saturated, or slightly superheated vapor (A, Figs. 93 and 94) is compressed adiabatically and reversibly to a superheated condition (B). The vapor is then cooled at constant pressure (BC) until liquefied. An expansion in a piston-cylinder mechanism is not required to lower the temperature of the medium since any process that reduces the pressure of a saturated liquid will reduce its temperature. Usually, the liquid at C flows through a restriction or throttling valve so that its pressure drops to the suction pressure of the compressor, but its temperature is still at C. This is an unstable condition, which cannot be represented by a point on the diagram. The internal energy of the liquid immediately after being throttled is greater than that of the saturated liquid at the lower pressure. Hence, the excess of energy causes violent boiling, which ceases as the equilibrium condition at D is attained.

The throttling or wiredrawing process is one of steady flow for which

$$H_C = H_D \tag{1}$$

since it is assumed to be adiabatic and the KE values are usually negligible. Thus, although a path cannot be drawn for the throttling process, the beginning and end points are on the same constant-H line. As a limiting case, the throttling process might consist of an infinite number of infinitesimal pressure drops with sufficient time at each pressure to permit the establishment of equilibrium throughout the process. Then, the path would follow the constant-H line passing through the initial point.

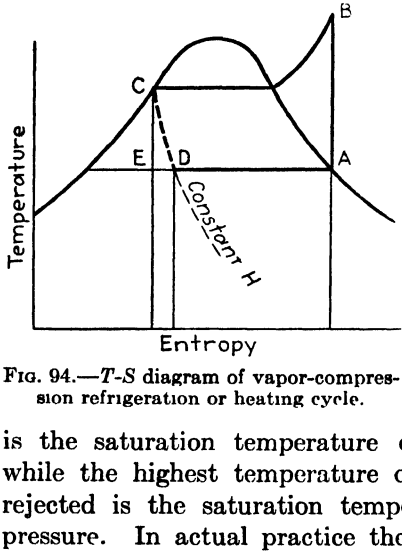

FIG. 94.—T-S diagram of vapor-compression refrigeration or heating cycle.

The lowest temperature of the cold body from which heat can be obtained is the saturation temperature corresponding to the suction pressure, while the highest temperature of the hot body to which heat can be rejected is the saturation temperature corresponding to the discharge pressure. In actual practice the cold body will be higher and the hot body lower in temperature than these limiting conditions. Thus, the condition at A is usually slightly superheated and at C is usually slightly subcooled. The heat absorbed during the cycle is

$$Q_{\text{in}} = (H_A - H_D) \tag{2}$$

since the process is one of constant pressure.

Also,
$$Q_{\text{out}} = (H_B - H_C) \tag{3}$$

The net work of the cycle is

$$W_{\text{in}} - W_{\text{out}} = Q_{\text{out}} - Q_{\text{in}} = (H_B - H_C) - (H_A - H_D) \tag{4}$$

and since
$$H_C = H_D$$

$$W_{\text{in}} - W_{\text{out}} = (H_B - H_A) \tag{5}$$

which is the same as the work of the compressor for a steady-flow analysis.

The use of an ideal expander at C would result in an isentropic expansion to E. The substitution of an expansion valve increases the work of the cycle by eliminating that of the expander. Also the *refrigerating effect* (the heat absorbed from the cold body) is reduced by an amount equivalent to the area under ED.

Example.—A vapor refrigeration cycle using ammonia as a medium operates between a cold body at 20 F and a hot body at 100 F. Determine the coefficient of performance as a refrigerating machine and the ideal horsepower to produce a ton of refrigeration per day.

Assuming the medium at A (Fig. 94) to be saturated,

$$H_A = 617.8 \text{ Btu/lb (Table IX, Appendix)}$$

also

$$S_A = 1.2969 \text{ Btu/(lb} \times {}^\circ\text{R)}$$

From Chart B, Appendix, at $S = 1.2969$ and $P = 211.9$ lb/in.² corresponding to the saturation temperature of 100 F

$$H_B = 710.8 \text{ Btu/lb}$$

Then

$$W_{\text{in}} = H_B - H_A = 710.8 - 617.8 = 93.0 \text{ Btu/lb of } NH_3$$

The refrigerating effect is

$$Q_{\text{in}} = H_A - H_D = 617.8 - 155.2 = 462.6 \text{ Btu}$$

The refrigerating coefficient of performance

$$= \frac{Q_{\text{in}}}{W_{\text{in}}} = \frac{462.6}{93.0} = 4.97$$

It requires the removal of 143.35 Btu/lb to freeze water at 32 F to ice at 32 F (see Table VI, Appendix). This is 1 lb of refrigeration. Thus, a ton of refrigeration per day is

$$\frac{2000 \times 143.35}{24 \times 60} = 199 \text{ Btu removed per min*}$$

The refrigerating coefficient of performance indicates 4.97 Btu removed per Btu of work input. Thus

$$200/(4.97 \times 42.4) = 0.95 \text{ hp/ton of refrigeration per day.}$$

Actually the horsepower required would be larger because of compressor friction and deviation from the ideal cycle.

"Dry-ice" Process and Cycle.—Dry ice or solid carbon dioxide is produced by expanding liquid CO_2 to a pressure in the solid-vapor region. Part of the liquid solidifies and the other part vaporizes during the process. The vapor is withdrawn from the solidification chamber, mixed with a fresh supply of CO_2 gas, compressed, cooled, and condensed to liquid, after which the expansion process is again repeated.

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* Usually 200 Btu/min is considered equivalent to 1 ton of refrigeration per day.

Inspection of the data of saturated CO_2 (Table XV and Chart C, Appendix) indicates that a pressure of about 70 atm is required to condense CO_2 with the average cooling-water temperature. Also, it will be noted that the pressure must be reduced to below 5 atm to produce solid CO_2 (Table XIV, Appendix).

The work of compression is reduced appreciably by multistage compression (see page 173) since the compression ratio is fairly high, being 70 to 1 for a suction pressure of 1 atm. However, this reduction in work is accomplished only if intercooling is used. Thus CO_2 vapor is compressed from A to B (Fig. 95) and then intercooled from B to C. This may be accomplished by transferring heat out of the compressed vapor by "bubbling" or flowing it (Fig. 96) through the liquid CO_2 which has been cooled to the temperature at M by a throttling process starting at J and ending at K. This results in the evaporation of some of the liquid and is indicated by the change in quality of the throttled mixture from K to L. The vapor formed by the throttling process and that formed by the intercooling process are added to the cooled vapor and all flow to the second-stage compressor.

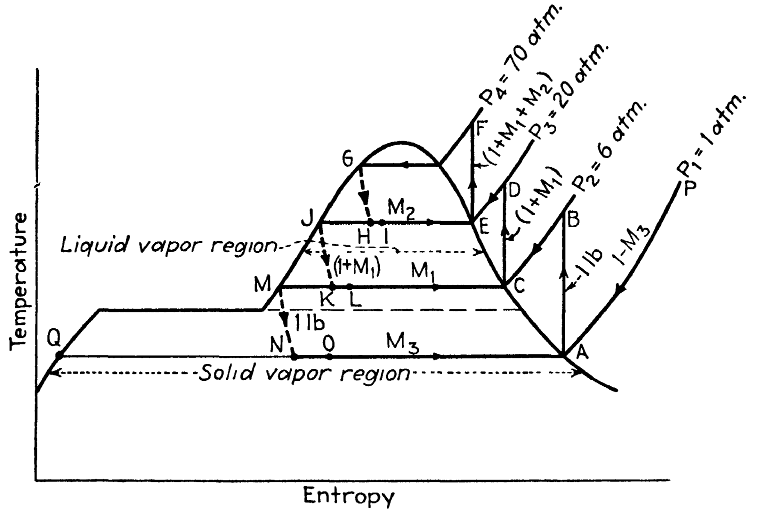

FIG. 95.—T-S diagram of a three-stage "dry-ice" compression cycle with intercooling.

After the second-stage compression, intercooling, etc., occur from D to E (Fig. 96) in a manner exactly the same as described for the first stage. After the third-stage compression, the available cooling-water supply (the hot body) is used to cool and condense the superheated vapor from F to G.

The three wiredrawing or throttling processes *GH*, *JK*, and *MN* cannot be represented by a path except in the ideal case for an infinitely slow process in which case equilibrium between pressure, temperature, and quality would be established as the pressure is slowly decreased.

Assuming that 1 lb of CO_2 is compressed in the first stage, the amount evaporated during the throttling process *JK* and that evaporated to cool 1 lb from *B* to *C*, making M_1 lb and indicated by the line *ML*, is added to the 1 lb from the first stage. Thus the second stage compresses $(1 + M_1)$ lb and has added to it M_2 lb evaporated in the throttling process *GH* and the evaporation process *HI*. Finally the third stage compresses $(1 + M_1 + M_2)$ lb of medium. This medium is then cooled and condensed to *G* and then is throttled to *H*.

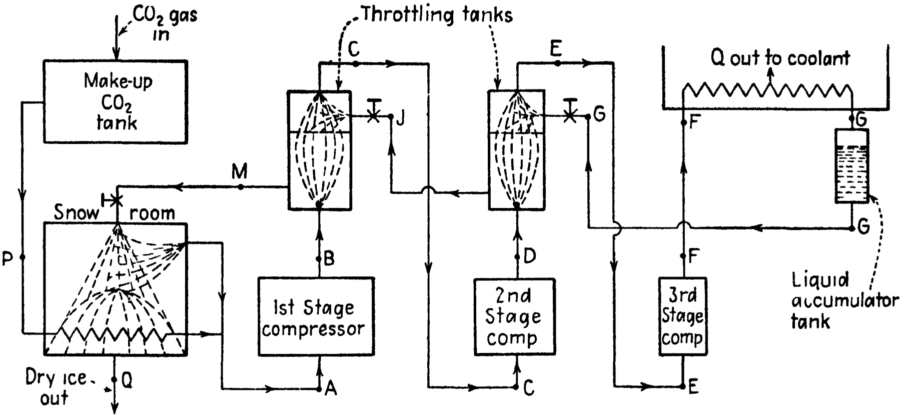

FIG. 96.—Flow diagram for three-stage compression "dry-ice" process.

Make-up medium is supplied at atmospheric pressure and temperature *P*. Some of the solid formed by the throttling process *MN* is evaporated and cools the make-up medium to the saturated condition *A*. This increases the quantity of vapor withdrawn from the solidifying chamber, the increase being indicated by the process *NO*. The net amount of solid formed is indicated by the length of the line *OA*, the length of the line *OQ* indicating the total vapor withdrawn. If M_3 is the total vapor withdrawn from the solidifying chamber, $(1 - M_3)$ is the amount of solid formed.

Then, the Energy Equation for the snow room (Fig. 96), assuming that the imaginary envelope around the room cuts the flow lines at *M*, *P*, *Q* and *A*, is

$$H_M + (1 - M_3)H_P = (1 - M_3)H_Q + H_A \qquad (1)$$

Also, the Energy Equation for the first-stage intercooler or throttling tank is

$$(1 + M_1)H_J + H_B = H_M + (1 + M_1)H_C \qquad (2)$$

and the Energy Equation for the second-stage intercooler is

$$(1 + M_1 + M_2)H_G + (1 + M_1)H_D = (1 + M_1)H_J + (1 + M_1 + M_2)H_E \quad (3)$$

Equation (1) may be solved for M_3, and solutions follow for M_1 and M_2 from Eqs. (2) and (3), respectively.

The total work required is the sum of the work values for each stage. These may be determined from a steady-flow analysis for each compressor process.

The dry-ice process, as described (Fig. 96), is not a cycle since gaseous CO_2 is flowing into the process and dry ice of the same amount is removed. If the supply of gaseous CO_2 is eliminated and sufficient heat is added to the solid CO_2 formed, in order to evaporate it to saturated vapor at condition A, all of the medium leaving the snow room will flow to the first-stage compressor and a cycle results. In this case the difference between the heat rejected to condense the CO_2 from F to G and the heat added to the dry ice* to evaporate it must equal the total work required for the compressors. This provides a check on the steady-flow work requirements for the compressors.

Example.—Determine the work per pound of dry ice produced by the three-stage compression process for the pressures and conditions indicated in Fig. 95. $T_P = 68$ F.

From Chart C or Tables XIV, XV, and XVI, Appendix, $H_M = -10.6$, $H_P = 169.0$, $H_Q = -113.0$, and $H_A = 133.3$ Btu/lb. Substituting these values into Eq. (1) results in

$$M_3 = 0.49 \text{ lb of vapor} \quad \text{and} \quad 1 - M_3 = 0.51 \text{ lb of solid}$$

Also, from the same sources,

$$H_J = 18.0, \quad H_B = 167.0, \quad \text{and } H_C = 136.1 \text{ Btu/lb}$$

Substituting these and the value for H_M into Eq. (2) results in a value of 0.50 lb of vapor for M_1.

Also, $H_G = 79.0$, $H_D = 158.5$, and $H_E = 138.9$ Btu/lb. Substituting these and the values for H_J and M_1 into Eq. (3) results in a value of 2.02 lb of vapor for M_2.

Thus for every pound of CO_2 condensed at 70 atm,

$$0.51 \div (1 + 0.50 + 2.02) = 0.145 \text{ lb of solid } CO_2 \text{ (dry ice)}$$

will be formed with this process.

The work of the first stage is

$$H_B - H_A = 167.0 - 133.3 = 33.7 \text{ Btu}$$

For the second stage,

$$(1 + M_1)(H_D - H_C) = 1.50(158.5 - 136.1) = 33.6 \text{ Btu}$$

---

* In this case the dry ice formed is indicated by the line NA, since the cooling of the make-up CO_2 has been eliminated.

For the third stage,

$$(1 + M_1 + M_2)(H_F - H_E) = 3.52(161.7 - 138.9) = 80.3 \text{ Btu}$$

Thus 147.6 Btu of work are required to produce 0.51 lb of dry ice. This is equivalent to 289.4 Btu of work per pound of dry ice formed.

Making the dry-ice process into a cycle

$$Q_{in} = (H_A - H_N) = 133.3 + 10.6 = 143.9 \text{ Btu}$$

since the process from N to O (Fig. 95) would be eliminated.

Also, $$Q_{out} = (1 + M_1 + M_2)(H_F - H_G) = 3.52(161.7 - 79.0) = 291.1 \text{ Btu}$$

$$\text{Total } W_{in} = Q_{out} - Q_{in} = 291.1 - 143.9 = 147.2 \text{ Btu}$$

This checks the work values obtained from the steady-flow analysis of the compressor processes.

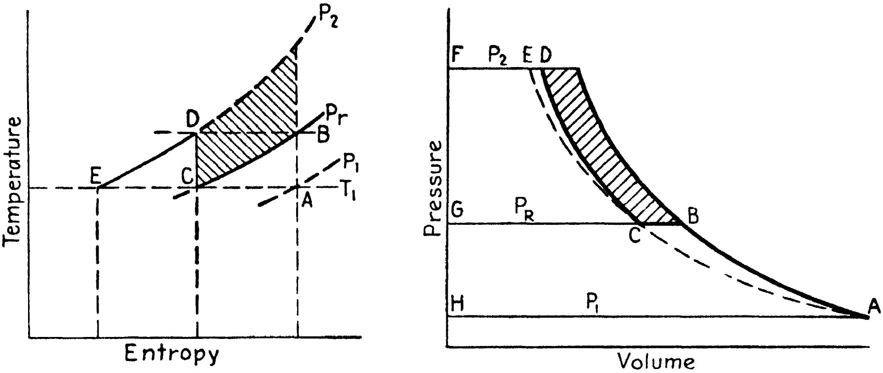

FIG. 97.—T-S and P-V diagrams of compression and cooling processes for two-stage compression

Multistage Compression and Intercooling.—The work of compression may be reduced appreciably by the use of several stages of compression with intercooling of the medium between each stage. In two-stage compression the medium is compressed adiabatically and reversibly, in the ideal case, from the initial or suction pressure to receiver pressure in the first stage (AB, Fig. 97). The medium is then discharged into a receiver in which it is cooled (BC) at constant pressure to some temperature at or near the initial temperature, it being described as perfect intercooling if cooled to the initial temperature. The medium is then compressed (CD) in the second stage from the receiver pressure to the discharge pressure after which it is discharged from the cylinder and cooled either in an aftercooler or by heat transfer from the tank or pipe line through which the medium flows.

The reduction in work because of two-stage compression and perfect intercooling is shown by the crosshatched areas in Fig. 97. These areas, indicating reduction in work required, approach zero as the receiver pressure approaches either the suction or the discharge pressure. Obviously, there must be some optimum receiver pressure, with perfect intercooling, for which the work required is a minimum.

The work of the first stage may be evaluated from the work area *ABGH* (Fig. 97) or by considering the compressor a steady-flow apparatus. Thus, $W_1 = H_B - H_A$, which for a gas with constant specific heats, becomes

$$= c_p(T_B - T_A) = c_pT_A\left(\frac{T_B}{T_A} - 1\right) = \text{const}\left[\left(\frac{P_r}{P_1}\right)^{\frac{k-1}{k}} - 1\right] \tag{1}$$

Likewise for the second stage,

$$W_2 = \text{const}\left[\left(\frac{P_2}{P_r}\right)^{\frac{k-1}{k}} - 1\right] \tag{2}$$

and since the constants are the same for both equations,

$$W_{\text{total}} = \text{const}\left[\left(\frac{P_r}{P_1}\right)^{\frac{k-1}{k}} + \left(\frac{P_2}{P_r}\right)^{\frac{k-1}{k}} - 2\right] \tag{3}$$

The optimum receiver pressure can be determined by differentiating this expression and equating the result to zero. This results in

$$P_r = (P_1 \times P_2)^{\frac{1}{2}} \tag{4}$$

But

$$\frac{T_B}{T_1} = \left(\frac{P_r}{P_1}\right)^{\frac{k-1}{k}} = \left(\frac{P_2}{P_1}\right)^{\frac{k-1}{2k}} \tag{5}$$

and

$$\frac{T_D}{T_1} = \left(\frac{P_2}{P_r}\right)^{\frac{k-1}{k}} = \left(\frac{P_2}{P_1}\right)^{\frac{k-1}{2k}} \tag{6}$$

Hence $T_B = T_D$, and for optimum receiver pressure and perfect intercooling the temperature rise in each stage should be the same. Also, the pressure ratios and work for both stages are the same.

Example.—Determine the optimum receiver pressure and stage-temperature ratio for a two-stage compression from 1 to 10 atm, with perfect intercooling.

$$P_r = (P_1 \times P_2)^{\frac{1}{2}} = (1 \times 10)^{\frac{1}{2}} = 3.16 \text{ atm}$$

For each stage,

$$\frac{T_{\text{discharge}}}{T_{\text{suction}}} = \left(\frac{10}{1}\right)^{\frac{0.4}{2.8}} = 1.389$$

Example.—Determine the optimum receiver pressures for a three-stage compressor, suction and discharge pressures being 1 and 70 atm, respectively.

For a two-stage compressor,

$$\text{Optimum receiver pr} = (\text{suction pr} \times \text{discharge pr})^{1/2}$$

The first two stages of a three-stage compressor have the second receiver pressure (P'') for the discharge pressure, P' for the receiver pressure, and P_1 for the suction pressure. Then

$$\text{Optimum first receiver pr} = P' = (P_1 \times P'')^{1/2}$$
$$\text{Optimum second receiver pr} = P'' = (P' \times P_2)^{1/2}$$

from which

$$P' = (P_1^2 P_2)^{1/3} = (1^2 \times 70)^{1/3} = 4.14 \text{ atm}$$

and

$$P'' = (P_1 P_2^2)^{1/3} = (1 \times 70^2)^{1/3} = 17.0 \text{ atm}$$

The foregoing relationships assume that the temperature of the medium being inducted into the compressor is that of the surrounding atmosphere which may be used for intercooling. Actually, cooling water usually somewhat lower in temperature is available and used. However, in the case of the gas refrigeration and heating cycle (Fig. 94), the compressor inducts the medium at atmospheric or lower temperatures, and it is not desirable to use the cold body for intercooling if refrigeration is to be obtained, or to intercool below the hot-body temperature if heating is the object of the cycle. Consequently, in applying the optimum receiver-pressure relations to the multistaging of the compression process for this cycle, the hot-body temperature should be considered as the initial temperature for the compression process, and the pressure of the medium at this temperature as the initial pressure for the compression process.

An infinite number of stages with perfect intercooling would result in the rejection of heat at the hot-body temperature with the minimum work of compression.

Multistage Expansion and Reheating.—Multistage-expansion engines are known as *compound* engines having high- and low-pressure stages, or as triple-expansion engines having high-, intermediate-, and low-pressure stages, etc. The advantage of multistage expansion with reheating has been shown in the case of the reheating cycle, page 161. It could be used to advantage in the case of the gas refrigeration and heating cycle (Fig. 92), by reheating to the cold-body temperature after each expansion process. An infinite number of expansion and reheating stages for this case would result in heat absorption from the cold body at its temperature and make the expansion work a maximum. Thus, as the number of stages of both compression and expansion is increased, with intercooling and reheating, respectively, the reversed Carnot cycle is approached as a limit. In practice, friction effects and multiplicity of apparatus make the use of many stages uneconomical.

Capacity of Reciprocating Engines.—The capacity of a reciprocating engine is the quantity of medium that flows through the machine per stroke, revolution, cycle, or unit of time. All reciprocating engines have a clearance space between the piston and the cylinder head when the piston is at the end of the exhaust stroke, and the medium always fills this space. If the exhaust valve on an engine closes with the piston in this position (dead center) (G, Fig. 98), the amount of medium in the clearance space at exhaust conditions would be trapped in the cylinder. At cutoff (point A), there is also a definite amount of medium in the cylinder. The amount admitted must be equal to the difference in the amount in the cylinder at cutoff and that which was trapped in the cylinder at exhaust-valve closure. Usually the exhaust valve closes at D (Fig. 98), trapping in the cylinder a larger volume of medium, at exhaust conditions, than that of the clearance volume.

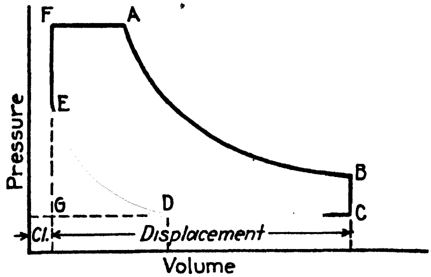

Fig. 98.—Engine indicator card.

Example.—A single-acting steam engine has a piston area of 1 ft^2 and a stroke of 1 ft. The exhaust valve closes at 80 per cent of the exhaust stroke, while cutoff occurs at 30 per cent of the expansion stroke. Exhaust-steam conditions are 15 $lb/in.^2$ abs pr and saturated. The condition at cutoff is 150 $lb/in.^2$ abs and 90 per cent quality. The clearance volume is 5 per cent of the displacement. Determine the capacity or steam consumption of the engine per revolution.

From Table VII at 150 $lb/in.^2$ pr, $V_g = 3.015$ and $V_f = 0.018\ ft^3$. Also at 15 $lb/in.^2$, $V_g = 26.29$.

The displacement of the engine is 1 ft^3. Hence volume A (Fig. 98) is equal to $0.30 \times 1 + 0.05 \times 1 = 0.35\ ft^3$.

The volume at D is $(1 - 0.80) \times 1 + 0.05 \times 1 = 0.25\ ft^3$.

The weight of the steam at A is $0.35\ ft^3 \div [3.015 - (1 - 0.90)2.997]\ ft^3/lb = 0.1292$ lb.

The weight of the steam at D is $0.25\ ft^3 \div 26.29\ ft^3/lb = 0.0095$ lb.

The amount of medium admitted per revolution is $0.1291 - 0.0095 = 0.1196$ lb

Volumetric Efficiency of Compressors.—The medium is compressed from A to B (Fig. 99), discharged from the cylinder from B to C, leaving the clearance volume filled with the medium at the discharge conditions. The medium trapped in the clearance volume is expanded to D when the piston reverses its motion, and more medium is admitted or flows into the cylinder from D to A. The amount admitted is the weight of the quantity $(V_A - V_D)$ of the medium at suction conditions, as well as the weight of the quantity $(V_B - V_C)$ at discharge conditions.

The path of the expansion process CD is assumed to be represented by the equation PV^n = constant in which n is usually assumed to be the same as for the compression curve. Then

$$V_D = V_C\left(\frac{P_C}{P_D}\right)^{\frac{1}{n}} \tag{1}$$

The volumetric efficiency is the ratio of the volume of the medium inducted per stroke, at the conditions in the reservoir or the atmosphere from which the compressor is abstracting medium, to the displacement of the compressor per stroke. The reservoir or ideal suction pressure is slightly above the cylinder suction pressure in order for flow to occur into the cylinder. Also, the temperature of the medium may change because of heat transfer to or from the cylinder walls during the flow of medium into the cylinder. First, neglecting these effects,

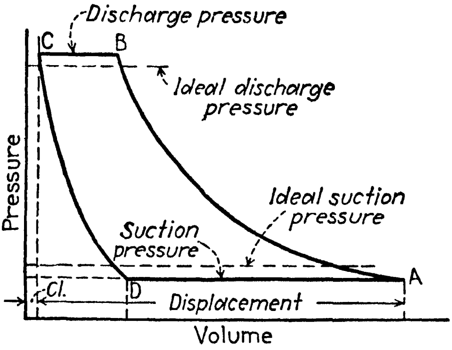

FIG. 99.—Compressor indicator card.

$$\text{Volumetric eff} = \frac{\text{vol inducted}}{\text{displacement}} = \frac{\text{disp} + \text{cl} - V_D}{\text{disp}} \tag{2}$$

or if the clearance is expressed as a ratio c, in terms of the displacement,

$$\text{Vol eff} = 1 + c - c\left(\frac{P_C}{P_D}\right)^{\frac{1}{n}} \tag{3}$$

The effect of change in pressure and temperature of the medium during induction can be introduced by the Equation of State or by the properties of the medium. If in the gaseous state,

$$\frac{V_{\text{reservoir}}}{V_{\text{inducted}}} = \frac{P_{\text{cyl}}T_{\text{res}}}{P_{\text{res}}T_{\text{cyl}}}$$

where reservoir indicates the condition of the medium before induction into the cylinder.

Thus,

$$\text{Vol eff} = \left[1 + c - c\left(\frac{P_C}{P_D}\right)^{\frac{1}{n}}\right]\frac{P_{\text{cyl}}T_{\text{res}}}{P_{\text{res}}T_{\text{cyl}}} \tag{4}$$

This relationship may be used to estimate the volumetric efficiency of a compressor when test data regarding actual quantity of medium inducted are not available.

Example.—An air compressor has a piston area of 1 ft^2 and a stroke of 1 ft. The clearance volume is 3 per cent of the displacement. The compressor inducts air at atmospheric pressure of 14.7 lb/in.^{2} into the cylinder and discharges it into a receiver where the pressure is 147 lb/in.^{2} abs. Determine the ideal volumetric efficiency and also the effect of 1 lb/in.^{2} differential at both suction and discharge conditions. $n = 1.33$.

$$\text{Ideal vol eff} = 1 + c - c\left(\frac{P_{\text{disch}}}{P_{\text{suction}}}\right)^{\frac{1}{n}} = 1 + 0.03 - 0.03\left(\frac{10}{1}\right)^{\frac{1}{1.33}} = 0.86$$

With 1 lb/in.^{2} differential at both suction and discharge conditions,

$$\text{Vol eff} = \left[1 + 0.03 - 0.03\left(\frac{148}{13.7}\right)^{\frac{1}{1.33}}\right]\frac{13.7}{14.7} = 0.79$$

Example.—Under actual test it was found that 1,000 ft^3 of air, measured at 14.5 lb/in.^{2} abs and 100 F, were inducted into the compressor in the foregoing example while 1,234 cycles occurred. The atmospheric conditions were 14.7 lb/in.^{2} pr and 100 F. Determine the actual volumetric efficiency.

The volume inducted under atmospheric conditions would be

$$V_{\text{atm cond}} = 1{,}000 \times \frac{14.5}{14.7} \times \frac{100 + 460}{100 + 460} = 987 \text{ ft}^3$$

$$\text{Vol eff} = \frac{\text{volume inducted}}{\text{displacement}} = \frac{987}{1{,}234} = 0.80$$

EXERCISES

1. A Carnot cycle operates between a source temperature of 1500°R and a refrigerator temperature of 500°R. The pressures at the beginning and end of the isothermal compression are atmospheric and 5 atm, respectively. Plot the cycle on both logarithmic and rectangular *P-V* and *T-S* coordinates for 1 lb of air.

2. Determine the net work out and heat into the Carnot cycle in Exercise 1. Also, check the thermal efficiency based on temperatures with that based on the work and heat values. *Ans.* Net work = 110.4 Btu.

3. A reversed Carnot cycle is used to heat a house in which a temperature of 70 F is to be maintained. The cold body from which the heat is received is the atmosphere which ranges from 0 to 60 F. Determine and plot the heating coefficient of performance against air temperature assuming a 10 F temperature difference for each heat-transfer process. Solve for 10 F intervals of temperature.

4. A Rankine cycle, using H_2O as a medium, has a back pressure of 15 lb/in.^{2} abs. Saturated vapor is supplied to the engine. Determine and plot the effect of varying the initial pressure from 200 to 3,000 lb/in.^{2} abs on the thermal efficiency of the cycle. *Ans.* 0.301 at 1500 lb/in.^{2}

5. A Rankine cycle, using H_2O as a medium, has initial conditions of 200 lb/in.^{2} abs and saturated vapor. Determine and plot the effect on thermal efficiency of decreasing the back pressure from 15 lb/in.^{2} to 1 in. Hg abs.

6. A Rankine cycle, using H_2O as the medium, has initial conditions of 200 lb/in.^{2} abs and saturated vapor, and a back pressure of 2 in. Hg abs.

a. Determine the ideal thermal efficiency.

b. Assume that friction during the expansion process reduces the *H* drop in the turbine to 0.80 of the ideal. Determine the net work and thermal efficiency.

c. Assume that 100 Btu of heat are added to the medium during a frictionless expansion process. Determine the net work and thermal efficiency.

d. The same as (*c*) except that the heat transfer is out.

e. The same as (*d*) except that sufficient friction occurs during the expansion so that the final entropy after is the same as before expansion.

f. Sketch all cycles on an *H-S* diagram.

7. Solve Exercise 4 for the incomplete expansion Rankine cycle having a volumetric expansion ratio between cutoff and release of 4 to 1.

8. Solve Exercise 5 for the incomplete expansion Rankine cycle having a volumetric expansion ratio between cutoff and release of 4 to 1.

9. A reciprocating steam pump receives steam theoretically at boiler pressure during the entire stroke, at the end of which the exhaust valve opens. Determine the thermal efficiency for the same conditions as in Exercise 4. Check the work solution by the equivalent of the indicator card area on the *P-V* diagram. Also sketch the cycle on an *H-S* diagram. *Ans.* 0.077 at 200 lb/in.^{2}

10. Georges Claude* proposed making use of the surface water in the tropical seas for the source of energy for a power plant, and the cold sea water at a depth of 3,000 ft for the cold body. The temperatures of these two bodies are approximately 80 and 40 F, respectively.

a. Make a diagrammatic sketch showing how the sea water will be used to develop power, indicating pressures at various points in the cycle.

b. Use any medium and compute the ideal Rankine cycle efficiency and ideal work output per pound of medium.

11. The Cochrane Corporation built a miniature power plant which operated on the wet- and dry-bulb temperature differences indicated by a psychrometer. Sketch a diagrammatic power plant and indicate how this effect can be utilized in this manner. Determine the ideal steam velocity in the turbine nozzle for atmospheric conditions of 100 F and 30 per cent relative humidity.

12. A single-stage regenerative cycle, with H_2O as the medium, operates between initial conditions of 200 lb/in.^{2} abs and saturated vapor, and a back pressure of 2 in. Hg abs. Determine the optimum bleeding pressure, the amount of medium to be bled, and the cycle efficiency. Use bleeding pressures of 200, 100, 50, 20, 14.7 lb/in.^{2} abs, 15 and 2 in. Hg abs, and plot the thermal efficiency and amount bled vs. bleeding pressure. Neglect feed-pump work. Sketch the cycle with optimum bleeding pressure on an *H-S* diagram. *Ans.* 0.132 lb bled and 0.318 eff at 20 lb/in.^{2} bleeding pr.

13. A single-stage reheating cycle operates between an initial pressure of 200 lb/in.^{2} abs and 750 F, and a back pressure of 2 in. Hg abs. The steam is reheated to 750 F. Determine the optimum reheating pressure for the cycle. Use reheating pressures ranging from initial to back pressure and plot the thermal efficiency vs. reheating pressure. Also, sketch the cycle with optimum reheat pressure on an *H-S* diagram.

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* Power from the Tropical Seas, *Mech. Eng.*, **52**, 1039 (1930).

14. Solve the binary example in the text assuming that the feed water is heated by waste heat (heat from the flue gases leaving the mercury boiler) to 400 F before entering the condenser boiler.

15. Assume that the mercury boiler in Exercise 14 is 80 per cent efficient before the waste-heat economizer is attached. Draw an imaginary envelope around the entire power plant, apply the Energy Equation to the process, and determine the power-plant efficiency for the example in the text and for Exercise 14.

16. A gas heating cycle with air as a medium is used to heat a house in which the temperature is to be maintained at 70 F. The cold body supplying heat to the medium is the atmosphere at 0 F. Assuming a 10 F terminal temperature difference for both heat-transfer processes, determine the coefficient of performance and compare with the result of Exercise 3 for the same conditions. Assume that T_B (Fig. 92) is 250 F. Sketch the cycle on an H-S diagram.

17. Recompute Exercise 16 for the same heat absorption from the atmosphere but rejecting the heat to the room by two stages with optimum receiver pressure for the first-stage heat rejection. Sketch the cycle on an H-S diagram.

18. Recompute Exercise 17 assuming heat absorption from the atmosphere in two stages with optimum reheating pressure for the expanders.

19. A reversed cycle uses a gas as a refrigerant. The gas is compressed isothermally, then expanded adiabatically and reversibly, and then absorbs heat at constant pressure until the initial condition is attained. Pressure rat o is 2 to 1.

a. Determine the refrigerating coefficient of performance.

b. Compare this with the Carnot coefficient of performance for the same hot and cold body temperatures as used in *a.*

20. An ammonia vapor refrigeration cycle is to be used for the manufacture of ice. The brine temperature is to be maintained at 10 F and cooling water is available at 80 F. A 10 F terminal temperature difference is required for both heat-transfer processes. Well water at 60 F is available for freezing into ice. Determine the quantity of ammonia circulated and the work required per ton of refrigeration per day; also determine the quantity of ice produced per day.

21. Kleinschmidt has developed a process for obtaining distilled water that has an energy requirement of only the work of compression of water vapor. The compressed water vapor heats and evaporates the impure H_2O which is then compressed. Assume that the liquid H_2O is supplied at 80 F and that the distilled H_2O is cooled at atmospheric pressure to the temperature of evaporation of the fresh supply.

a. Determine the required suction pressure of the ideal compressor to result in a steady-flow process.

b. Determine the ideal work per pound of distilled H_2O.

c. Determine the ideal compressor size to produce 1 lb of distilled H_2O per hr, if the bore and stroke are equal and the compressor speed is 300 rpm.

d. Make the series of processes into a cycle and check the work by cycle analysis.

Ans. *a.* 5 lb/in.^{2}; *b.* 52 Btu.

22. Two-stage compression with intercooling is to be used for the cycle in Exercise 20. The compressed vapor is desuperheated by bubbling through the throttled liquid from the high-pressure stage (see the Dry-ice Process). All of the vapor from the throttling and the desuperheating process is added to the vapor from the first stage and all is compressed in the second stage. Determine the quantity of ammonia circulated and the work required per ton of refrigeration per day; also determine the quantity of ice produced per day. Determine the optimum receiver pressure and final results by assuming various pressures and plotting the results vs. receiver pressure. Also, sketch the cycle on an H-S diagram.

23. Recompute the dry-ice example in the text using single-stage compression, the make-up being cooled by evaporation of solid CO_2 to a saturated condition. Compare the work required and the amount of dry ice produced per pound of CO_2 circulated.

24. Recompute the dry-ice example in the text without intercooling but with constant pressure mixing of the vapor formed by each throttling process and that discharged from the compressor stage at the same pressure. Determine the pounds of solid CO_2 formed per pound of CO_2 condensed after the last stage of compression. Also, determine the work requirement and the theoretical displacement of the low-pressure stage per pound of solid CO_2 formed.

25. Estimate the displacement per pound of medium flowing to the reciprocating engine in Exercise 7, for 200 lb/in.^{2} initial pressure. Compression occurs at 70 per cent of the return stroke. Clearance is 5 per cent of the displacement.

26. Estimate the displacement per pound of ammonia flowing to the ammonia compressor in Exercise 20. Clearance volume is 2 per cent of the displacement.

27. Estimate the displacement of both expanders in Exercise 18, for 1 lb of NH_3 flowing to the low-pressure stage. Clearance volume is 2 per cent of the displacement.

CHAPTER IX

THE COMBUSTION PROCESS

Combustion.—The rather rapid reaction between a fuel and oxygen that results in the liberation of chemical energy is termed *combustion.* The combustion process is used to liberate the energy supplied to the boiler in the steam-power-plant process, to liberate the energy supplied to the internal-combustion engine, and to liberate energy for various heating processes.

The oxygen supply for the combustion process is usually obtained from the atmosphere which introduces nitrogen and other gases into the process. However, the nitrogen and other gases are usually assumed to be inert substances which do not alter the reaction between the fuel and oxygen.

Air.—The principal constituents of air are oxygen and nitrogen and seven other gases of which argon and carbon dioxide are of sufficient quantity to require consideration in refined computations. The relationship of the constituents by volume and by weight is shown in the accompanying table.

Constituents	Symbol	Mol wt	Vol analysis*	Relative wt†	Approx vol analysis	Relative vol	Approx wt analysis	Constituents
Oxygen. . . .	O_2	32	0.2099	6.717	0.21	1	0.23	Oxygen
Nitrogen .	N_2	28	0.7803	21.861	0.79	3.76	0.77	Nitrogen and other gases
Argon.	A	40	0.0094	0.376				
Carbon dioxide.	CO_2	44	0.0003	0.013				
Other gases. . .			0.0001					
Total (air). . . .	.		1.0000	28.97	1.00	4.76	1.00	

* "International Critical Tables," Vol. I, 393, McGraw-Hill Book Company, Inc., New York, 1926.

† Using the accurate molecular weights.

The approximate volume analysis, $0.21O_2$ and $0.79(N_2$ and other gases), will be used in dealing with air in reaction equations, and the symbol N_2 will indicate nitrogen and other gases as shown in the table. However, the internal energy, enthalpy, etc., of N_2 will be used since very little error is introduced at high temperatures and practically none at low temperatures.

Reaction Equations.—The principal fuels used in the combustion process are carbon and hydrogen and their combinations known as *hydrocarbons*, such as octane, C_8H_{18}. There are also the alcohols, such as ethyl alcohol, C_2H_6O, which consist of combinations of carbon, hydrogen, and oxygen. The elementary reaction equations for carbon and hydrogen uniting with oxygen are as follows:

$$C + O_2 \rightleftharpoons CO_2 \tag{1}$$

$$2H_2 + O_2 \rightleftharpoons 2H_2O \tag{2}$$

Thus, 1 molecule of carbon unites with 1 molecule of oxygen and forms 1 molecule of carbon dioxide, and 2 molecules of hydrogen unite with 1 molecule of oxygen and form 2 molecules of H_2O. Since a mole of any substance is a fixed number of molecules, the reaction equations may be read in terms of moles as well as of molecules.

If all the substances in reaction equations are assumed to be gaseous and at the same pressure and temperature, the moles can be read as volumes in any system of dimensions. Thus, Eq. (2) may be read,

$$2 \text{ ft}^3 \text{ of } H_2 + 1 \text{ ft}^3 \text{ of } O_2 \rightleftharpoons 2 \text{ ft}^3 \text{ of } H_2O$$

The dimensions of a reaction equation may be changed from moles to weight in pounds by multiplying the moles of each constituent by its respective molecular weight. Thus, Eq. (2) becomes,

$$4 \text{ lb of } H_2 + 32 \text{ lb of } O_2 \rightleftharpoons 36 \text{ lb of } H_2O$$

Obviously, the sum of the weights of the reacting mixture constituents always equals the sum of the weights of the products in any reaction equation. This is not true for the moles or volumes of mixture and products. However, the same number of molecules of each element such as C, H_2, O_2, and N_2, either alone or combined with others, will be found on both sides of a correct reaction equation.

Since air contains 3.76 ft³ of N_2 (and other gases) for each cubic foot of O_2, there will be 3.76 moles of N_2 introduced into the reaction equation for each mole of O_2 required when the reaction occurs with air. Thus, the combustion of C and H_2 in air results in the following equations:

$$C + O_2 + 3.76N_2 \rightleftharpoons CO_2 + 3.76N_2 \tag{3}$$

and

$$2H_2 + O_2 + 3.76N_2 \rightleftharpoons 2H_2O + 3.76N_2 \tag{4}$$

The interpretations regarding weight, volume, and moles for these reactions are obviously the same as indicated heretofore.

Reactions may occur with more O_2 or air than required for complete combustion. Denoting the excess moles of O_2 by e, the reaction equation for a hydrocarbon is

$$C_nH_m + \left(n + \frac{m}{4} + e\right)O_2 + 3.76\left(n + \frac{m}{4} + e\right)N_2 \rightarrow$$
$$nCO_2 + \frac{m}{2}H_2O + eO_2 + 3.76\left(n + \frac{m}{4} + e\right)N_2 \quad (5)$$

H_2O in Products of Combustion.—Fuels that contain hydrogen have H_2O as one of the products of combustion. Immediately after the reaction, the H_2O is highly superheated vapor which approaches and passes through the saturated condition as the products of combustion cool. The temperature at which the H_2O will be saturated vapor is called the *dew point* (see Chap. VI). The products of combustion are usually rejected from such apparatus as boilers and internal-combustion engines at a temperature above the dew point. However, further cooling of the products will eventually result in the condensation of at least some of the H_2O formed during the reaction.

The partial pressure of any gas in a mixture of perfect gases is directly proportional to the number of moles of that constituent. The water vapor may be assumed to act as a perfect gas at low pressures and its partial pressure determined from the molal relationship. Inspection of the water-vapor tables for the saturation temperature corresponding to the partial pressure of the H_2O indicates the dew point for the water vapor.

Example.—Determine the dew point for the water in the products of combustion from the reaction of H_2 with the required air. The products are cooled at a constant pressure of 14.7 lb/in.² abs. The reaction equation is

$$2H_2 + O_2 + 3.76N_2 \rightleftharpoons 2H_2O + 3.76N_2$$

$$\text{pp of } H_2O = \frac{2 \text{ moles of } H_2O}{5.76 \text{ moles of products}} \times 14.7 \text{ lb/in.}^2 = 5.10 \text{ lb/in.}^2$$

Inspection of Table VI or VII, Appendix, indicates a saturation temperature or dew point of 163 F corresponding to this pressure.

For high water-vapor partial pressures the assumption of perfect-gas condition introduces appreciable error. In this case the dew-point temperature may be assumed. This indicates the partial pressure of the water vapor, from which the partial pressure of the noncondensable constituents can be determined if the total pressure is known. The volume of the noncondensable constituents, determined from the Equation of State for perfect gases, should be the same as the volume of the saturated water vapor at the correct dew-point temperature. If the volume of the space occupied by the water vapor is known, the specific volume (V_g) indicates the dew-point temperature.

Analysis of Products of Combustion.—The products of complete combustion of common fuels are CO_2 and H_2O. Some CO, H_2, CH_4, and O_2 will be found in the products if the combustion is incomplete, and considerable O_2 will be present if an excess of it is supplied. Also, N_2 will always be present if air is used for the combustion process.

An analysis of the products of combustion may be made with an *Orsat apparatus* which permits the selective absorption of some of the products (CO_2, CO, and O_2). The products are passed through or brought into contact with a potassium hydroxide solution which will absorb CO_2 only; then through a pyrogallic acid solution which will absorb the O_2; and finally through a cuprous chloride solution which will absorb the CO. The remainder consists of N_2 and other gases. The contraction in volume is noted in each case and indicates the volumes or moles of each constituent per unit volume or mole of the products analyzed, exclusive of the water vapor in the products. The products analysis for a given fuel may be predicted from the reaction equation, written in terms of moles, if the completeness of combustion is known or is assumed.

Example. Determine the maximum percentage of CO_2 in the products of combustion of carbon and the required air; also for the combustion of CH_4 and the required air.

The maximum CO_2 will occur with complete combustion. The reaction equation for carbon is

$$1C + 1O_2 + 3.76N_2 \rightleftharpoons 1CO_2 + 3.76N_2$$

$$100 \times \frac{1CO_2}{4.76 \text{ prod}} = 21.0\% \ CO_2$$

The reaction equation for CH_4 is

$$1CH_4 + 2O_2 + 7.52N_2 \rightarrow 1CO_2 + 2H_2O + 7.52N_2$$

$$100 \times \frac{1CO_2}{8.52 \text{ dry prod}} = 11.7\% \ CO_2$$

The gases when inducted into the Orsat apparatus for analysis are usually saturated with water vapor. The absorption of one of the constituents, at constant total pressure, raises the partial pressure of the remaining constituents. The water vapor cannot have a higher partial pressure than that corresponding to the temperature. The contraction in volume when one of the gases is absorbed causes the condensation of enough water vapor to maintain a constant water-vapor pressure. Thus, the water vapor does not influence the Orsat analysis which is the dry-gas analysis.

Example.—Assume a mixture of $0.20CO_2$, $0.10H_2O$, and $0.70N_2$ is drawn into an Orsat apparatus and analyzed at atmospheric pressure. Prove that there would be a 22.2 per cent contraction of volume when the CO_2 is absorbed.

The partial pressure of the water vapor is initially 0.1 atm, which indicates a mixture temperature of 115 F which will be assumed to be the Orsat temperature. After CO_2 absorption, the water-vapor pressure will still be 0.1 atm, which makes the partial pressure of the N_2 equal to 0.9 atm.

Assuming the initial total volume to be 100, which is also the volume of the N_2 at its initial partial pressure of 0.7 atm, the N_2 volume at 0.9 atm will be

$$\frac{0.7}{0.9} \times 100 = 77.8 \text{ vol}$$

Thus, there would be a contraction in volume of 22.2 per cent when the CO_2 is absorbed.

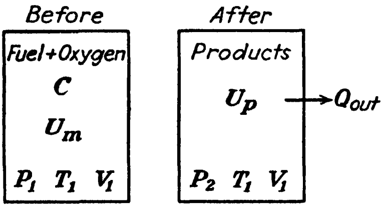

FIG. 100.—Constant-volume calorimeter process.

Chemical Energy and Heat Value.—The chemical energy and heat value of a fuel are determined from the reaction of the fuel and oxygen in the presence of excess oxygen in a constant-volume or constant-pressure calorimeter.* The products of combustion are cooled to the initial temperature of the mixture.† The Energy Equation for the constant-volume calorimeter process, Fig. 100, is

$$C + U_m = U_p + Q_{\text{out}} \tag{1}$$

or

$$C = Q_V + (U_p - U_m)_T \tag{2}$$

where subscripts m and p indicate fuel-oxygen mixture and products, respectively.

Q_V is the heat value of the fuel for the constant-volume calorimeter process. It is an absolute value but varies with temperature as indicated by $(U_p - U_m)_T$. Obviously, when this term is zero, the chemical energy and heat values are identical.

The constant-pressure calorimeter usually has steady flow‡ of mixture into the apparatus and steady flow of products out of it, sufficient heat being transferred out to reduce the temperature of the products to that of the mixture before reaction. The Energy Equation for this process (Fig. 101) is

$$C + U_m + PV_m = U_p + PV_p + Q_{\text{out}} \tag{3}$$

or

$$C = Q_P + (H_p - H_m)_T \tag{4}$$

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* For a comprehensive analysis of the bomb-calorimeter process, see *Nat. Bur. Stand., Jour. Res.*, **10**, 525 (1933).

† The cooling bath surrounding the constant-volume bomb rises a few degrees in temperature, for which a correction is made.

‡ Flow indicates pressure drop and velocities. However, the pressure drops are small and the kinetic energy effects are usually negligible.

Q_P is the heat value of the fuel for the constant-pressure calorimeter process. It is an absolute value but varies with temperature as indicated by $(H_p - H_m)_T$. Thus, heat values vary with the process and the temperature of the process.

Example.—The heat value reported per mole of CO is 121,721 Btu (Table XXIV, Appendix). This was obtained at a constant pressure of 1 atm and a temperature of 77 F for the reaction

$$(CO)_g + 0.5(O_2)_g \rightleftharpoons (CO_2)_g$$

where subscript g indicates the gaseous state. Determine the chemical energy per mole of CO for the foregoing reaction.

The Energy Equation for this process is

$$C_{CO+0.5O_2} + (H_{CO} + 0.5H_{O_2})_{536.6} = (H_{CO_2})_{536.6} + Q_P$$

Substituting values from Table XIX, Appendix, results in

$$C_{CO+0.5O_2} + 1147 + 574 = 1181 + 121{,}721$$
$$C_{CO+0.5O_2} = 121{,}181 \text{ Btu/mole}$$

Chemical energy values are relative values and must be used only with the tables of internal energy or enthalpy values from which they are evaluated.* Chemical energy values would be absolute values if E and H values were on an absolute basis.

Internal energy and enthalpy values based on the same datum plane as values for gaseous mediums are used in evaluating chemical energies since the data for gaseous mediums are known for high temperatures and can be used for all combustion processes.

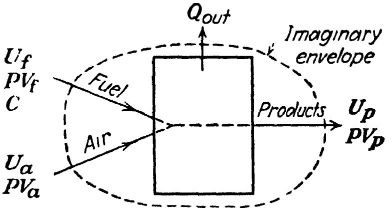

Fig. 101.—Constant-pressure calorimeter process.

Fuels containing H_2 react with O_2 and form H_2O as one of the products. The humidity of the air or oxygen, pressure, temperature, and nature of the process determine the amount of H_2O condensed during the process. Under certain conditions, the amount of water condensed may be more than that formed. Calorimetric processes for the determination of heat value are usually conducted under conditions that result in the conden-

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* Absolute values of energy should be substituted in Eqs. (1) to (4) for U_m and U_p. Such values are not available, and it is inferred that constants U_m^0 and U_p^0 are included, which if added to the tabulated values would result in absolute values.

Thus for Eq. (1), $C + (U_m + U_m^0) = (U_p + U_p^0) + Q_{out}$

or $(C + U_m^0 - U_p^0) = Q_V + (U_p - U_m)_T$

Values of chemical energy as determined in the preceding example and given in Table XXIV, Appendix, are actually values of $(C + U_m^0 - U_p^0)$. Obviously, substituting these *apparent* chemical energy values in an energy equation and making use of the same internal energy tables will eliminate the constants U_m^0 and U_p^0.

sation of all or nearly all the water formed. Results are reported on the basis that all the water formed has been condensed.*

Example.—The heat value reported per mole of H_2 is 122,963 Btu. This was obtained at a constant pressure of 1 atm and a temperature of 77 F for the reaction

$$(H_2)_g + 0.5(O_2)_g \rightleftharpoons (H_2O)_l$$

when subscripts g and l represent gaseous and liquid states, respectively. Determine the chemical energy per mole of H_2.

The Energy Equation for this process is

$$C_{H_2+0.5O_2} + (H_{H_2} + 0.5H_{O_2})_{536.6} = [(H_{H_2O})_l]_{536.6} + Q_P$$

Substituting values from Table XIX (Appendix),

$$C_{H_2+0.5O_2} + 1146 + 575 = 1167 - 18.016 \times 1050.4\dagger + 122{,}963$$
$$C_{H_2+0.5O_2} = 103{,}485 \text{ Btu/mole}$$

Chemical energy and heat values for various fuels are given in Table XXIV (Appendix).

Heat value represents the heat transfer out of the calorimeter process operated under specified conditions. It is not an energy term in the energy equation for a combustion process at conditions other than those of the calorimeter process. Chemical energy, however, is a function of the mediums undergoing reaction. Any two substances that will react have associated with them a definite amount of chemical energy for the given reaction. This can be used as an energy term in the Energy Equation for the given reaction process. Since heat value and chemical

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[*] This is commonly termed the "high heat value." A purely fictitious low heat value is obtained by assuming that the H_2O is not liquid but is saturated vapor. This condition could not exist unless the calorimeter process was operated at a temperature corresponding to or higher than the dew point for the water vapor in the products of the reaction.

The difference between the high and the low heat values for H_2 at 77 F is $18.016 \times 1050.4 = 18{,}924$ Btu/mole of H_2, where 1050.4 is the latent heat for 1 lb of H_2O at 77 F.

Then, Low heat value = 122,963 − 18,924 = 104,039 Btu/mole

The principal argument for the use of low heat value is that the internal-combustion engine and gas turbine exhaust the products of combustion at temperatures well above the dew-point temperature for the water vapor and, therefore, the engine and turbine should be charged with the low heat value. However, the mere fact that the engine and turbine fail to return the products to the original mixture temperature is an indication of inefficiency, and the engine and turbine should be charged with the high heat value in efficiency determinations.

[†] The latent heat of H_2O is subtracted from the enthalpy value from Table XIX, Appendix, at the same temperature, to get the enthalpy value for liquid water on the same basis as the values in Table XIX.

energy are related through the Energy Equation for the calorimeter process [Eqs. (1) to (4)], heat value may be introduced by substituting for $C + (U_m)_{T_1}$ in the Energy Equation its equal $(Q_V + U_p)_{T_1}$ (page 193), or by substituting for $C + (H_m)_{T_1}$ its equal $(Q_P + H_P)_{T_1}$.

The fuel, as well as the H_2O, may be liquid or gaseous for the calorimeter or other combustion process. Tables XIX and XX, Appendix, contain values of internal energy for various mediums in the gaseous state. Energy values for mediums in the liquid state should have the same datum plane so that the chemical energies of the various reactions will be the same regardless of the state of the fuel. Thus energy values of liquid fuels are obtained by subtracting the latent heat of the fuel, which is known at some given temperature, from the energy value of the fuel in the gaseous state at the same temperature. This procedure is based on the assumption that the energy value in the gaseous state is the same as the value of the saturated vapor at the same temperature. This is very nearly correct at low pressures.

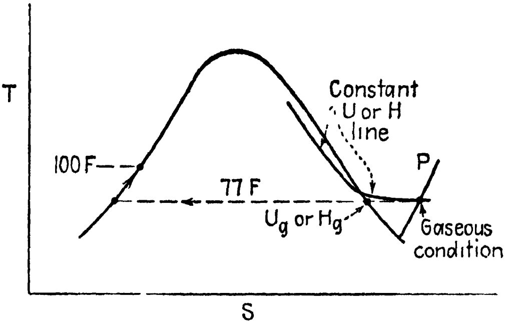

FIG. 102.—Illustrating method of evaluating U_g or H_g from gaseous data.

When the energy value at the saturated-liquid line at some temperature has been determined, the value at the desired temperature can be obtained by the use of the specific heat of the liquid fuel and the temperature difference between the desired temperature and that at which the energy value is known.

Example.—Determine the internal energy of 1 mole of liquid octane at 100 F. Assume the specific heat of liquid octane to be 0.5 Btu/(lb × °F temp diff).

The latent heat of 1 mole of octane at 77 F is 17,730 Btu (Table XXIV).

The enthalpy of gaseous octane at 77 F is 674 + 1066 = 1740 Btu/mole (Table XX).

The difference in H_f between 100 and 77 F is $0.5 \times 114 \times (100 - 77) =$ 1311 Btu/mole.

Thus, following the path indicated in Fig. 102,

$$H_f = 1740 - 17730 + 1311 = -14679 \text{ Btu/mole}$$

The difference between the heating values at constant pressure and constant volume can be determined from the difference between Eqs. (2) and (4). Thus,

$$Q_P - Q_V = [(H - U)_m - (H - U)_p]_T \tag{5}$$

$$= [(PV)_m - (PV)_p]_T \tag{6}$$

Assuming that all constituents are in the gaseous state,

$$Q_P - Q_V = (M_m - M_p)RT \tag{7}$$

From Eq. (6) it is obvious that the difference between the two heating values is the work done by or on the products in expanding or contracting during the constant-pressure process. From Eq. (7) it is obvious that, if the mixture and products of the reaction are in the gaseous state and equal in moles, the two heating values are the same.

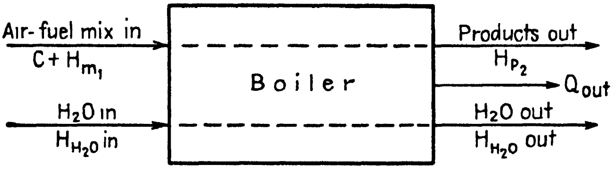

FIG. 103 —The boiler process.

Boiler Process.—The boiler furnace is supplied with a mixture of fuel and air that has a definite amount of internal energy. The chemical energy of the reaction is liberated by the combustion process and appears as energy of the products of combustion. Most of the energy liberated is transferred from the products of combustion to the medium (usually water) that is evaporated in the boiler. A considerable amount of energy leaves with the products of combustion which are not cooled to the initial mixture temperature, and some energy is radiated from the boiler setting. An appreciable amount of energy may leave with the ash in the form of unliberated chemical energy and internal energy. Since the mediums flow to and from the boiler, flow work is associated with them.

Assuming complete combustion, no loss in the ash, and a steady-flow process, the Energy Equation for this process (Fig. 103) is

$$C + H_{m_1} + H_{H_2O_{in}} = H_{p_2} + H_{H_2O_{out}} + Q_{out} \tag{1}$$

or

$$(H_{out} - H_{in})_{H_2O} = C + H_{m_1} - H_{p_2} - Q_{out} \tag{2}$$

This equation indicates the enthalpy increase for the H_2O flowing through the boiler.

Example.—A boiler is burning CH_4 with 25 per cent excess air. The flue-gas temperature leaving the boiler is 440 F. Determine the pounds of water vapor produced per mole of CH_4, assuming 3 per cent loss of chemical energy by radiation from the boiler setting. Feed-water temperature is 200 F and the steam leaves the boiler saturated at a pressure of 150 lb/in.² abs. CH_4 and air are supplied at 77 F.

The reaction equation for the combustion process is

$$CH_4 + 2.5O_2 + 9.40N_2 \rightarrow CO_2 + 2H_2O + 0.5O_2 + 9.40N_2$$

From Table XIX, Appendix,

$$\begin{aligned} H_{p_2} &= (H_{CO_2} + 2H_{H_2O} + 0.5H_{O_2} + 9.40H_{N_2})_{900} \\ &= 4752 + 8306 + 1888 + 34{,}705 = 49{,}651 \text{ Btu} \end{aligned}$$

Also, from Table XIX, Appendix,

$$\begin{aligned} H_{m_1} &= (H_{CH_4} + 2.5H_{O_2} + 9.40H_{N_2})_{536.6} \\ &= 1178 + 2873 + 10{,}782 = 14{,}833 \end{aligned}$$

Then, $$H_{p_2} - H_{m_1} = 49{,}651 - 14{,}833 = 34{,}818 \text{ Btu/mole of } CH_4$$

The chemical energy of $CH_4 + O_2$ per mole of CH_4 is 345,214 Btu, Table XXIV, Appendix. The energy lost by heat transfer from the boiler setting is 3 per cent of the chemical energy. Hence,

$$Q_{out} = 0.03 \times 345{,}214 = 10{,}356 \text{ Btu}$$

Substituting the foregoing values in Eq. (2) results in

$$\begin{aligned} (H_{out} - H_{in})_{H_2O} &= 345{,}214 - 34{,}818 - 10{,}356 \\ &= 300{,}040 \text{ Btu/mole of } CH_4 \end{aligned}$$

From Tables VI and VII, Appendix,

$$\begin{aligned} H_{in} &= 168.0 \text{ Btu/lb of feed water} \\ H_{out} &= 1194.1 \text{ Btu/lb of steam} \end{aligned}$$

Then, $$\frac{300{,}040}{1194.1 - 168.0} = 292.4 \text{ lb of } H_2O\text{/mole of } CH_4$$

Complete-combustion Temperatures.—The maximum temperature for the combustion process will be attained with a constant-volume, adiabatic, and complete-combustion process, assuming no energy supply other than that of the reaction. The Energy Equation for this process is

$$C + (U_m)_1 = (U_p)_2 \tag{1}$$

All the chemical energy of the reaction and the internal energy of the mixture appear as internal energy of the products of combustion. This indicates the maximum temperature of the combustion process. If work is done on the mediums or some other form of energy is added during the combustion process, it will increase the energy of the products and also the final temperature.

Example.—Determine the temperature of the products of combustion of carbon monoxide with oxygen if the process occurs at constant volume with no heat loss. Initial mixture temperature is 60 F.

The reaction equation is

$$CO + 0.5O_2 \rightleftharpoons CO_2$$

The Energy Equation for this process is

$$C_{CO+0.5O_2} + (U_{CO} + 0.5U_{O_2})_{520} = (U_{CO_2})_T$$

Substituting values from Tables XIX and XIV, Appendix,

$$121{,}181 + 0 + 0 = (U_{CO_2})_T$$
$$(U_{CO_2})_T = 121{,}181 \text{ Btu}$$

This is well above the internal energy of CO_2 at 5400°R; and since an appreciable amount of CO_2 will dissociate at this temperature, any estimate of final temperature by extrapolation of the internal-energy values would be worthless.

The use of air instead of oxygen, in the foregoing example, appreciably reduces the final temperature of the products of combustion, since the energy is divided between the nitrogen and the products formed by the reaction.

Example.—If the required air instead of oxygen is used in the previous example, the reaction equation becomes

$$CO + 0.5O_2 + 1.88N_2 \rightleftharpoons CO_2 + 1.88N_2$$

The Energy Equation for this reaction is

$$C_{CO+0.5O_2} + (U_{CO} + 2.38U_{air})_{520} = (U_{CO_2} + 1.88U_{N_2})_T$$

Substituting values from Tables XIX and XXIV, Appendix, results in

$$(U_{CO_2} + 1.88U_{N_2})_T = 121{,}181 + 0 + 0 = 121{,}181 \text{ Btu}$$

The left side of this equation is solved for various values of T, as follows:

T, °R	U_{CO_2}	$1.88U_{N_2}$	Sum
5200	53,963	54,447	108,410
5300	55,265	55,738	111,003
5400	56,569	57,034	113,603

Extrapolating for 121,181 Btu total energy results in a final temperature of about 5700°R. An appreciable amount of CO_2 would dissociate at this temperature and, therefore, it could not be attained.

The constant-pressure combustion process has work out during the reaction and results in a lower final temperature. The Energy Equation for this process with no heat loss is

$$C + (U_m)_1 = (U_p)_2 + W_{\text{out}} \qquad (2)$$
$$= (U_p)_2 + P[(V_p)_2 - (V_m)_1]$$

or
$$C + (H_m)_1 = (H_p)_2 \qquad (3)$$

Example.—Determine the temperature of the products of combustion of CO with the required air if the process occurs at constant pressure with no heat loss. $T_1 = 60$ F.

The reaction equation for this process is

$$CO + 0.5O_2 + 1.88N_2 \rightleftharpoons CO_2 + 1.88N_2$$

The Energy Equation is

$$C_{CO+0.5O_2} + (H_{CO} + 2.38H_{\text{air}})_{520} = (H_{CO_2} + 1.88H_{N_2})_T$$

Substituting values from Tables XIX and XXIV, Appendix, results in

$$(H_{CO_2} + 1.88H_{N_2})_T = 121{,}181 + 1033 + 2.38 \times 1033$$
$$= 124{,}673 \text{ Btu}$$

The left side of this equation is solved for several T values as follows:

T, °R	H_{CO_2}	$1.88H_{N_2}$	Sum
4700	56,817	65,574	122,391
4800	58,308	67.223	125,531

Interpolating for 124,673 Btu results in a final temperature of 4773°R. Appreciable dissociation of CO_2 would occur at this temperature and, therefore, it could not be attained.

Other combustion processes with heat transfer and dilution with other gases are solved in a similar manner. Complete combustion cannot occur unless heat loss or some other means of energy dissipation reduces the energy content of the products to a condition of about 3000°R, below which dissociation is usually negligible. Chemical equilibrium must be considered above this temperature.

The chemical energy term may be eliminated from the foregoing equations in the following manner in the constant-volume process:

$$C + (U_m)_1 = (U_p)_2 \qquad \text{Eq. (1), p. 191}$$

The constant-volume calorimeter equation is

$$C + (U_m)_1 = (U_p)_1 + (Q_V)_1 \qquad \text{Eq. (1), p. 186}$$

Eliminating C between these equations results in

$$(Q_V)_1 = (U_2 - U_1)_p \qquad (4)$$

Thus, if the fictitious process of burning the fuel at T_1 to obtain $(Q_V)_1$ is followed, and if this heat is used to raise the *products* from T_1, the correct final temperature for the products will result. The actual process that starts with fuel and oxygen or air at T_1 and proceeds to products at T_2 is lost sight of in this method of analysis.

Heat values must be used for combustion calculations for fuels such as coal and commercial petroleum products for which the internal-energy values are unknown. However, the foregoing indicates that the products of combustion must be known.

Example.—The initial temperature in the preceding example is 60 F. The heat value of CO at 60 F is

$$\begin{aligned} Q_P &= C_{CO+0.5O_2} + (H_m - H_p)_{60} \\ &= 121{,}181 + 1.5 \times 1033 - 1033 = 121{,}698 \text{ Btu/mole} \end{aligned}$$

The Energy Equation for the combustion process in the preceding example is

$$C_{CO+0.5O_2} + H_{m_1} = H_{P_2} = Q_{P_1} + H_{P_1}$$

Thus, $$Q_{P_1} = (H_T - H_{520})_P = (H_p)_T - 2.88 \times 1033$$

there being 2.88 moles of products.

Finally, $$(H_p)_T = 121{,}698 + 2975 = 124{,}673 \text{ Btu}$$

This is the same result that was obtained in the preceding example.

Chemical Equilibrium.—The maximum temperatures attained in combustion processes are appreciably lower than those based upon complete combustion, because of heat loss and dissociation of the products of combustion. Appreciable dissociation occurs at high temperatures and is accompanied by an absorption of internal energy which is transformed into chemical energy. Thus, the dissociated products will have chemical energy associated with them, and the net chemical energy liberated appears as internal energy or enthalpy of the products and as heat loss.

Hydrocarbon fuels burn to CO_2 and H_2O which appear in the products along with N_2 when air is used as the oxidizing agent. Dissociation results in the formation of appreciable quantities of CO, H_2, and O_2, according to the reversible reactions

$$2CO_2 \rightleftharpoons 2CO + O_2 \tag{1}$$

$$2H_2O \rightleftharpoons 2H_2 + O_2 \tag{2}$$

Other constituents such as N, O, H, OH, NO, and C may be formed by further dissociation and combination of the various constituents.

Both combination of the various constituents into products of combustion and dissociation of the products are assumed to occur simultaneously in various parts of the mixture at chemical-equilibrium conditions, but the net result of the combination processes is exactly equivalent to the dissociation processes if the temperature remains constant. Writing the CO reaction equation for combustion or combination and then dissociating to chemical equilibrium conditions result in

$$2CO + O_2 \rightleftharpoons 2CO_2 \rightleftharpoons 2xCO + 2(1 - x)CO_2 + xO_2 \qquad (3)$$

when x represents the part of the CO_2 that has been dissociated into CO and O_2. The H_2 reaction would be

$$2H_2 + O_2 \rightleftharpoons 2H_2O \rightleftharpoons 2yH_2 + 2(1 - y)H_2O + yO_2 \qquad (4)$$

Similarly, for a hydrocarbon,

$$C_nH_m + \left(n + \frac{m}{4}\right)O_2 \rightarrow nCO_2 + \frac{m}{2}H_2O \rightleftharpoons nxCO + n(1 - x)CO_2 + \frac{m}{2}yH_2 + \frac{m}{2}(1 - y)H_2O + \left(\frac{n}{2}x + \frac{m}{4}y\right)O_2 \qquad (5)$$

The Second Law of Thermodynamics indicates that irreversible processes result in an increase in entropy for the entire system undergoing change. The combustion process when started by a source of ignition is a self-acting process that is irreversible. Self-acting processes will attain an equilibrium condition when the entropy of the system is a maximum. Consequently, to determine the equilibrium condition for the products of combustion, the expression for the entropy of the products of reaction (and any other medium involved) as indicated by the x (or y) relations must be differentiated with respect to x (or y) and equated to zero to determine the equilibrium condition.

For any products constituent (Eq 3, p. 105)

$$MS = M\int c_p\frac{dT}{T} - MR\ln pp + MS_{0_{T,P}} \qquad (6)$$

when S_0 is the constant of integration for the T and P functions here used.

Applying this relation to the products of the CO reaction (Eq. 3), noting that the partial pressure of any constituent is proportional to the ratio of the moles of that constituent to the total moles,

$$\begin{aligned} S_{\text{prod}} = {} & 2x\int c_{p_{CO}}\frac{dT}{T} + 2(1 - x)\int c_{p_{CO_2}}\frac{dT}{T} + x\int c_{p_{O_2}}\frac{dT}{T} \\ & -R\left[2x\ln\frac{2x}{2+x}P + 2(1-x)\ln\frac{2(1-x)}{2+x}P + x\ln\frac{x}{2+x}P\right] \\ & + \left[2xS_{0_{CO}} + 2(1-x)S_{0_{CO_2}} + S_{0_{O_2}}\right]_{T,P} \end{aligned} \qquad (7)$$

wherein P is the total pressure of the gases.

Assume that the temperature and the total pressure of the products will be constant for any increment change of x. If x, the fraction dissociated, is decreased, chemical energy will be liberated and heat must be transferred out to maintain constant temperature. In order not to introduce the effect of the heat-transfer process on entropy, a reversible process will be used. This indicates the use of a large body at temperature T to or from which heat may be transferred without changing the net entropy of the system. The amount of heat transferred when $2x$CO changes to $2(x + dx)$CO is $dxQ_{P_{2CO}}$, wherein $Q_{P_{2CO}}$ is the heat of combustion at constant pressure at temperature T for the given reaction. For an increment of dx increase in x, $dxQ_{P_{2CO}}$ heat must be transferred from the large body at temperature T, resulting in a decrease in entropy of the large body of

$$-dS = \frac{dxQ_{P_{2CO}}}{T} \tag{8}$$

or

$$\frac{dS}{dx} = -\frac{Q_{P_{2CO}}}{T} \tag{9}$$

Differentiating the various parts of Eq. (7) results in the following.

$$\frac{dS}{dx} \text{ for } c_P \frac{dT}{T} \text{ terms} = 2\int c_{P_{CO}}\frac{dT}{T} + \int c_{P_{O_2}}\frac{dT}{T} - 2\int c_{P_{CO_2}}\frac{dT}{T} \tag{10}$$

$$\frac{dS}{dx} \text{ for } S_0 \text{ terms} = 2S_{0_{CO}} + S_{0_{O_2}} - 2S_{0_{CO_2}} \tag{11}$$

Also dS/dx for the ln P terms is obtained as follows:

$$\begin{aligned}\frac{d}{dx}\left[2x \ln \frac{2x}{2+x} P\right] &= \frac{d}{dx}\left[2x \ln 2x - 2x \ln (2+x) + 2x \ln P\right] \\ &= 2 + 2 \ln 2x - \frac{2x}{2+x} - 2 \ln (2+x) + 2 \ln P \qquad (12)\end{aligned}$$

$$\frac{d}{dx}\left[2(1-x) \ln \frac{2(1-x)}{2+x} P\right] = -2 - 2 \ln 2(1-x) - \frac{2(1-x)}{2+x} + 2 \ln (2+x) - 2 \ln P \tag{13}$$

$$\frac{d}{dx}\left[x \ln \frac{x}{2+x} P\right] = 1 + \ln x - \frac{x}{2+x} - \ln(2+x) + \ln P \tag{14}$$

Adding Eqs. (12) to (14),

$$\frac{d}{dx} (\ln P \text{ terms}) = \ln \frac{(2x)^2 \cdot xP}{[2(1-x)]^2(2+x)} \tag{15}$$

Noting that $(2 + x) = M_p$ = total moles and multiplying numerator and denominator by P^2/M_p^3 result in

$$\frac{d}{dx} (\ln P \text{ terms}) = \ln \frac{\left(\frac{2x}{M_p} P\right)^2 \left(\frac{x}{M_p} P\right)}{\left[\frac{2(1-x)}{M_p} P\right]^2} \tag{16}$$

$$= \ln \frac{(\mathrm{ppco})^2\, \mathrm{ppo}_2}{(\mathrm{ppco}_2)^2} = \ln K_{P_{2CO_2}} \tag{17}$$

where $K_{P_{2CO_2}}$ is the equilibrium constant for the given reaction and is defined by the partial pressures of the constituents at equilibrium.

Adding Eqs. (10) and (11) and noting that the sum of the respective terms is the entropy of the various constituents for a unit pressure for each constituent, result in

$$(2S_{CO} + S_{O_2} - 2S_{CO_2})_{\text{unit pr}} = (S_{\text{mix}} - S_{\text{prod}})_{\text{unit pr}} = \Delta S \tag{18}$$

Adding the various parts of the foregoing differentiation,

$$\frac{dS}{dx} = \frac{Q_{P_{2CO}}}{T} + S_{\text{mix}} - S_{\text{prod}} - R \ln K_{P_{2CO_2}} = 0 \tag{19}$$

for a maximum and for equilibrium

or
$$T(S_{\text{mix}} - S_{\text{prod}})_{\text{unit pr}} = T\,\Delta S = Q_{P_{2CO}} + RT \ln K_{P_{2CO_2}} \tag{20}$$

It should be noted that

1. ΔS is the entropy of reaction, $S_{\text{mix}} - S_{\text{prod}}$, for the reaction considered with each constituent at a unit pressure and temperature T.
2. Q_P is the heat of combustion at constant pressure and temperature T for the reaction considered.
3. K_P is the equilibrium constant (Eq. 17) for the reaction considered. The partial pressures of the constituents formed by dissociation are in the numerator and the partial pressures of the original constituents are in the denominator. The exponents of the partial pressures are the coefficients of the terms in the elementary reaction equation [Eq. (1)]. Thus, multiplying the coefficients of the various terms in a reaction equation by n increases the value of ln K_P by the nth power, etc.

Also, simplification of Eq. (16) results in only one P/M_p term, the power to which it is raised being equal to difference in the moles of constituents on the right and left sides of the elementary reaction Eq. (1).

Tables XXV and XXVI, Appendix, contain data for various reactions.

The dissociation of $2H_2O$ is indicated by a reaction equation [Eq. (2)] similar to that for the dissociation of $2CO_2$. Consequently, the equilibrium constant is identical in form (see Table XXV, Appendix). The symbol y instead of x may be used for the H_2O reaction.

Subtracting the $2H_2O$ reaction from the $2CO_2$ reaction results in the water gas reaction. Thus,

$$\begin{array}{c} 2CO_2 \rightleftharpoons 2CO + O_2 \\ \underline{2H_2O \rightleftharpoons 2H_2 + O_2} \\ 2CO_2 + 2H_2 \rightleftharpoons 2CO + 2H_2O \end{array}$$

Since the equilibrium constant is the ratio of the product of the partial pressures of the constituents on one side to the product of the partial pressures on the other side of the equation, it can be shown that

$$K_{P_{wg}} = \frac{x(1 - y)}{y(1 - x)} = \frac{K_{P_{2CO_2}}}{K_{P_{2H_2O}}} \tag{21}$$

Example.—Check the equilibrium constant at 5000°R for the reaction

$$2CO_2 \rightleftharpoons 2CO + O_2$$

by using Eq. (20). Note in the following that the first and second conditions for the entropy and Energy Equations are indicated by the right and left sides, respectively, of the reaction equation.

From Tables XXII and XXV, Appendix, at 5000°R and a unit pressure for each constituent,

$$S_2 - S_1 = 2\int_{520}^{5000} c_{P_{CO}}\frac{dT}{T} + \int_{520}^{5000} c_{P_{O_2}}\frac{dT}{T} - 2\int_{520}^{5000} c_{P_{CO_2}}\frac{dT}{T} + \Delta S_{520}$$

$$= 35.44 + 18.49 - 55.96 + 41.42 = 39.39$$

The Energy Equation for the heat of combustion is

$$C + (H)_1 - (H)_2 = (C_{2CO+O_2} + H_{2CO} + H_{O_2}) - (H_{2CO_2}) = Q_{P_{2CO}}$$

From Tables XIX and XXIV, Appendix, at 5000°R,

$$242{,}362 + (55{,}824 + 19{,}860) + (29{,}616 + 9930) - (102{,}730 + 19{,}860) = Q_P$$

or

$$Q_P = 235{,}002$$

Substituting in Eq. (19),

$$\log_{10}K_{P_{2CO_2}} = \frac{5000 \times 39.39 - 235{,}002}{1.986 \times 5000 \times 2.3026} = -1.67$$

which is slightly lower than the value listed in Table XXVI, Appendix.

At high pressures, mediums deviate appreciably from the perfect-gas state, and the partial pressures in Eq. (17) must be replaced by the fugacities or the activities (fugacities in atm.).*

Chemical-equilibrium Combustion Temperatures.—The maximum temperatures attained during combustion processes depend on the dissociation of the products of the reaction. For reactions such as

$$2CO + O_2 \rightleftharpoons 2CO_2$$

there will be two unknowns, T, the maximum temperature, and x, the part dissociated. The expression for $K_{P_{2CO_2}}$, which depends on temperature, provides one relationship between these two variables. Thus, from Eq. (16), page 196,

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* ELWELL, R. H., Calculation of Chemical Equilibrium at High Pressures, *Ind. and Eng. Chem.*, **32**,147 (1940).

$$K_{P_{2CO_2}} = \frac{x^3}{(1-x)^2}\frac{P}{M_p} \tag{1}$$

where $M_p = 2 + x$ = total moles of substances at equilibrium for this reaction. This equation is used for constant-pressure processes.

Assuming gaseous constituents and perfect-gas relationships,

$$\frac{P_1V_1}{M_1T_1} = \frac{PV}{M_pT} \tag{2}$$

where subscript 1 represents the conditions at the beginning of the process. Eliminating P/M_p between Eqs. (1) and (2) results in the equilibrium equation for the constant-volume case. Thus

$$\frac{K_{P_{2CO_2}}}{T} = \frac{x^3}{(1-x)^2}\frac{P_1}{M_1T_1}\frac{V_1}{V} \tag{3}$$

The Energy Equation for the process of combustion of CO with O_2, assuming a condition of chemical equilibrium for the products, provides another relationship involving the two variables T and x. The simultaneous solution of Eq. (3) and the Energy Equation provides a solution for the two unknowns.

Example.—Determine the temperature of combustion of carbon monoxide with air if the process occurs at constant volume with no heat transfer. Initial mixture temperature and pressure are 60 F and 1 atm.

For this constant-volume process, Eq. (3) may be written

$$\log\frac{x^3}{(1-x)^2} = \log K_{P_{2CO_2}} - \log T + \log\frac{6.76 \times 520}{1}$$

where $M_1 = 2$ moles CO + 1 mole O_2 + 3.76 moles of N_2,

$P_1 = 1$ atm,

and $T_1 = 520°R$.

For every assumed value of T, a value of K_P for the dissociation of CO_2 can be obtained from Table XXVI, Appendix, and the right side of this equation can be evaluated and plotted (Fig. 104). Values of the left side are determined for various values of x. These are also plotted in Fig 104, the same vertical ordinate being used since the left side equals the right side. Corresponding values of T and x can be read from this diagram and plotted as the Equilibrium Equation in Fig. 105.

The Energy Equation for this process becomes

$$\begin{aligned}2(1-x)C_{CO+O_2} &+ (2U_{CO} + U_{O_2} + 3.76U_{N_2})_{520} \\ &= [2xU_{CO} + 2(1-x)U_{CO_2} + xU_{O_2} + 3.76U_{N_2}]_T\end{aligned}$$

Substituting values of C_{CO+O_2} and U_{520} in the left side and values of U at various assumed temperatures in the right side of this equation provides values of T and x that satisfy the Energy Equation. Thus, at 5000°R,

$$2(1 - x)121{,}181 + (0) = 55{,}824x + 2(1 - x)51{,}365 + 29{,}616x + 3.76 \times 27{,}589$$

or
$$x = 0.159$$

Plotting values of T and x obtained in the foregoing manner results in the curve labeled Energy Equation in Fig. 105. The intersection with the curve labeled Equilibrium Equation indicates a solution at $T = 4900°\text{R}$ and $x = 0.183$.

The N_2 energy term in the foregoing solution is eliminated when the combustion occurs with O_2 alone. The partial-pressure expression for K_P is the same, since, with air, the partial pressure of the N_2 appears in both the numerator and denominator and cancels itself. However, the value of M_1 in the equilibrium equation is affected.

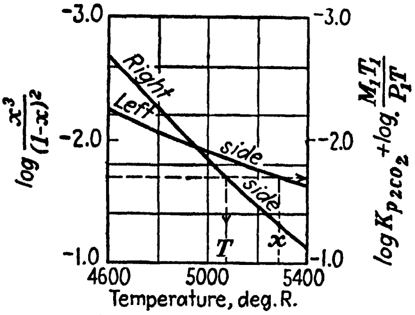

FIG. 104.—Solution of Equilibrium Equation for $2CO + O_2 \leftrightharpoons 2CO_2$ reaction

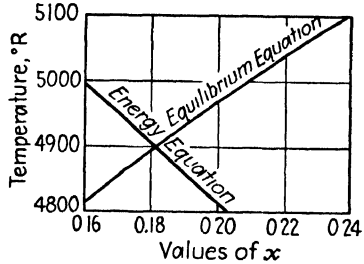

FIG. 105.—Solution for $2CO + O_2 \leftrightharpoons 2CO_2$ reaction.

Combustion processes dealing with hydrocarbons, as indicated in Eq. (5), page 195, have three unknowns, T, x, and y. The Energy Equation for the process provides one relationship between these unknowns. The equilibrium expressions for the dissociation of CO_2 and H_2O, applied to the equilibrium mixture for the given process, provide two other relationships between the three unknowns. The simultaneous solution of these equations provides a solution for the combustion process.

The solution may be made by evaluating the Energy Equation for an assumed temperature which provides a relation between x and y. The combination of the two equilibrium relationships for the dissociation of CO_2 and H_2O, *applied to this reaction,* results in the equilibrium relationship for the water-gas reaction, Eq. (21), page 198. Substituting the values of $K_{P_{wg}}$ for the assumed temperature provides another relationship between x and y, which combined with that of the Energy Equation at the same assumed temperature results in the evaluation of x and y at this temperature. The assumed value of T and the determined values of x and y must satisfy either one of the equilibrium relationships applied to this reaction, and provides a check on the assumed temperature.

Example.—Determine the temperature of constant-volume adiabatic combustion for C_8H_{18} and the required air. Initial temperature is 1100°R. Initial pressure is 125 lb/in.^{2} abs.

The reaction equation is

$$C_8H_{18} + 12.5O_2 + 47N_2 \rightarrow 8xCO + 8(1 - x)CO_2 + 9yH_2 + 9(1 - y)H_2O + (4x + 4.5y)O_2 + 47N_2$$

The Energy Equation for this reaction is

$$C_{C_8H_{18}+12.5O_2} + (U_{mix})_{1100} = (U_{prod})_T + 8xC_{CO+0.5O_2} + 9yC_{H_2+0.5O_2}$$

From Table XXIV, Appendix,

$$C_{C_8H_{18}+12.5O_2} = 2{,}201{,}618, \quad 8xC_{CO+0.5O_2} = 969{,}448x, \quad \text{and} \quad 9yC_{H_2+0.5O_2} = 931{,}365y \text{ Btu}$$

From Tables XIX and XX, Appendix, at 1100°R.

$$U_{C_8H_{18}} + 59.5U_{air} = 32{,}241 + 175{,}942 = 208{,}183 \text{ Btu}$$

From Table XIX, Appendix, at 5000°R:

Products	Numerical terms	x terms	y terms
$8xCO$		223,256x	
$8(1 - x)CO_2$	410,920	−410,920x	
$9yH_2$			232,371y
$9(1 - y)H_2O$	358,965		−358,965y
$(4x + 4.5y)O_2$		118,464x	133,272y
$47N_2$	1,296,683		
Sum	2,066,568	− 69,200x	6,678y

Substituting the various values in the Energy Equation results in

$$2{,}201{,}618 + 208{,}183 = 2{,}066{,}568 - 69{,}200x + 6{,}678y + 969{,}448x + 931{,}365y$$

or

$$y = 0.3659 - 0.9597x \qquad (A)$$

At 5000°R, for the water-gas reaction (Table XXV, Appendix),

$$K_{p_{wg}} = 6.547 = \frac{x(1 - y)}{y(1 - x)}$$

or

$$y = \frac{x}{6.547 - 5.547x} \qquad (B)$$

Eliminating y between Eqs. (A) and (B) and solving the resulting quadratic equation result in

$$x = 0.313$$

and, from Eq. (A),

$$y = 0.065$$

These values have been plotted in Fig. 106.

The equilibrium relationship for the dissociation of CO_2 is applied to this combustion process as follows:

$$K_{P_{2CO_2}} = \frac{[CO]^2[O_2]}{[CO_2]^2} = \frac{\left(\frac{8x}{M_p}P\right)^2\left(\frac{4x + 4.5y}{M_p}\right)P}{\left[\frac{8(1-x)}{M_p}P\right]^2} = \frac{x^2}{(1-x)^2}(4x + 4.5y)\frac{P}{M_P} \qquad (C)$$

Substituting the determined values for x and y and values for P_1T/M_mT_1, the equivalent of P/M_p, results in

$$K_{P_{2CO_2}} = \frac{(0.313)^2}{(1 - 0.313)^2}(1.252 + 0.293)\frac{125 \times 5000}{14.7 \times 60.5 \times 1100} = 0.203$$

From Table XXVI, Appendix, $K_{P_{2CO_2}}$ at 5000°R = 0.0200, which does not check the foregoing computed value. The correct and computed values for K_P are plotted in Fig. 106. Assuming other values of T and following the foregoing procedure result in a solution at T = 5220°R, x = 0.216, and y = 0.010.

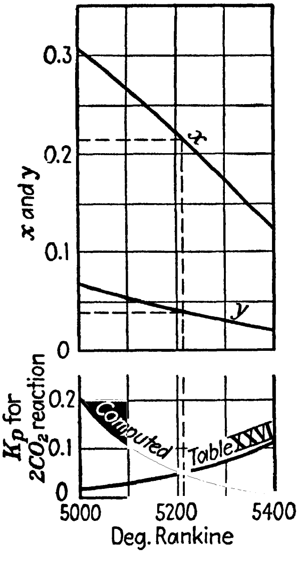

FIG. 106—Solution for C_8H_{18}-air reaction.

Reversible Adiabatic Expansion or Compression.

Reversible Adiabatic Expansion or Compression.—Mediums undergoing reversible adiabatic processes do not have a change in entropy. Consequently, these processes are analyzed by determining the final temperature T_2 or other condition that will indicate the same entropy at the end as at the beginning of the process.

Either the volume ratio V_2/V_1 or pressure ratio P_2/P_1 is known. Then, for any assumed T_2, the equilibrium constants are known and the corresponding values of x and y can be determined. This determines the moles of the constituents at T_2. The partial pressure of each constituent is determined by the characteristic equation for the corresponding T_2, V_2 (or P_2), and M_2. Finally the entropy S_2 is determined by the entropy equation from the determined moles, partial pressures, and assumed temperature.

Example.—The combustion of a mixture of C_8H_{18} and the required air at an initial temperature of 1100°R and an initial pressure of 125 lb/in.^{2} abs resulted in a temperature of 5220°R, x = 0.216, and y = 0.040. The mixture is to be expanded reversibly and adiabatically to five times the volume corresponding to the volume for the initial conditions given. Determine the final conditions and the work done.

The total moles of products of combustion are

$$8xCO + 8(1 - x)CO_2 + 9yH_2 + 9(1 - y)H_2O + (4x + 4.5y)O_2 + 47N_2$$

or, substituting the values of x and y,

$$1.728CO + 6.272CO_2 + 0.36H_2 + 8.64H_2O + 1.044O_2 + 47N_2 = 65.044 \text{ moles}$$

These products resulted from 60.5 moles of a mixture of C_8H_{18} and air.

$$V_1 = \frac{M_pRT_1}{P_p} = \frac{M_mRT_m}{P_m} = \frac{60.5 \times 1545 \times 1100}{125 \times 144} = 5710 \text{ ft}^3$$

Hence $V_2 = 5V_1 = 28{,}550 \text{ ft}^3$.

Assume T_2	3800°R	3900°R	4000°R	$T_1 = 5220$
$\log_{10} K_{P_{wg}}$ (Table XXVI).	0.693	0.709	0.723	
$K_{P_{wg}}$.	4.932	5.116	5.284	
$\log_{10} K_{P_{2CO_2}}$ (Table XXVI)	−4.95	−4.59	−4.25	
$K_{P_{2CO_2}}$	1.122×10^{-5}	2.571×10^{-5}	5.624×10^{-5}	
y from $K_{P_{wg}}$[Eq. (B) p. 201]	$\frac{x}{4.932 - 3.932x}$	$\frac{x}{5.116 - 4.116x}$	$\frac{x}{5.284 - 4.284x}$	
x*.	0.0281	0.0365	0.0467	0.216
y.	0.0058	0.0074	0.0092	0.040

---

* Determined by substituting the value for y in terms of x into Eq. (C), p. 202, and for P/M_p its equal RT_2/V_2 or $(1545 \times T_2)/(28{,}550 \times 14.7 \times 144)$, and evaluating x for the corresponding value of K_{P2CO_2}. Note that P is in atmospheres.

Then from Tables XXII and XXV, Appendix, adding ΔS_{520} for the respective reactions to the fuel constituents,

$8x\int c_{p_{CO}} \frac{dT}{T}$.	8.1	10.6	13.6	67.0
$8(1 - x)\int c_{p_{CO_2}} \frac{dT}{T}$. . . .	185.9	186.7	188.0	179.4
$9y\int c_{p_{H_2}} \frac{dT}{T}$.	1.3	1.7	2.1	10.0
$9(1 - y)\int c_{p_{H_2O}} \frac{dT}{T}$.	169.8	172.3	174.0	198.5
$(4x + 4.5y)\int c_{p_{O_2}} \frac{dT}{T}$. . .	2.2	2.9	3.7	19.8
$47\int c_{p_{N_2}} \frac{dT}{T}$.	712.1	723.0	733.1	842.0
$\Sigma\int Mc_p \frac{dT}{T}$.	1079.4	1097.2	1114.5	1316.7

The $-MR$ ln pp terms for the entropy expression are determined as follows for the constituents at 5220°R, where,

$$P = \frac{P_m}{M_m}\ \frac{M_pT}{T_m} = \frac{125 \times 65.044 \times 5220}{14.7 \times 60.5 \times 1100} = 43.4 \text{ atm}$$

Constituent	$pp = \frac{M}{65.044} \times 43.4$ atm	ln pp†	$-1.986M$ ln pp
$1.728CO$	1.151	0.1407	−0.48
$6.272CO_2$	4.178	1.4298	−17.81
$0.360H_2$	0.240	−1.4271	1.02
$8.640H_2O$	5.756	1.7502	−30.03
$1.044O_2$	0.695	−1.3639	2.83
$47.000N_2$	31.320	3 4442	−321.50
$65.044 = M_p$	$43.340 = P$	....	$-365.97 = \Sigma MR \ln pp$

In a similar manner the $-MR$ ln pp terms for the assumed values of T_2 are obtained with the following results:

Assumed T_2	3800°R	3900°R	4000°R	$T_1 = 5220$
$\Sigma \int Mc_p \frac{dT}{T}$	1079.4	1097.2	1114.5	1316 7
ΣMR ln pp*.............	−132.4	−133.7	−136.0	−366 0
S_2	947 0	963 5	978.5	S_1 = 950.7

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* The determination of the partial pressures in atmospheres indicates that the values of $\int c_p \frac{dT}{T}$ in Table XXII are assumed to be the entropies at a pressure of 1 atm.

Plotting the values of S_2 for the corresponding values of T_2 indicates a solution where $S_2 = S_1$ at 3820°R. At this condition $x_2 = 0.0297$ and $y_2 = 0.0061$.

The work done in a nonflow reversible adiabatic expansion is indicated by the Energy Equation for the process.

$$W_{out} = (U + C)_1 - (U + C)_2$$

Evaluating this equation for $T_2 = 3820$°R and $T_1 = 5220$°R,

$T_1 = 5220$°R			$T_2 = 3820$°R		
Constituent	U_1	C_1	Constituent	U_2 at 3820°R	C_2
$1.728CO$	50,848	209,401	$0.238CO$	4,734	28,842
$6.272CO_2$	340,087	. . ....	$7.762CO_2$	281,372	
$0.360H_2$	9,828	37,248	$0.055H_2$	998	5,692
$8.640H_2O$	365,551	....	$8.945H_2O$	244,344	
$1.044O_2$	32,800	....	$0.146O_2$	3,070	
$47.000N_2$	1,367,606	....	$47.000N_2$	922,563	
65.044	2,166,720	246,649	64.142	1,457,081	34,534

$$\begin{aligned} W_{\text{out}} = (U + C)_1 - (U + C)_2 &= 2{,}413{,}3.9 - 1{,}491{,}615 \\ &= 921{,}754 \text{ Btu}/59.5 \text{ moles of air} \\ &= 535 \text{ Btu/lb of air} \end{aligned}$$

Combustion Charts.—The foregoing combustion solutions neglected the dissociation of O_2, N_2, and H_2 into their respective atoms and the formation of OH and NO. The inclusion of these constituents requires more relationships, which complicates the analysis. The solution of problems dealing with C_8H_{18} or fuels having the same (or nearly the same) carbon-hydrogen ratio when reacting with various percentages of required air has been simplified by the construction of diagrams, such as Chart I, from which the thermodynamic properties of the equilibrium mixture can be obtained. The method* used to compute the points for these diagrams is as follows:

The four kinds of atoms present (C, H, O, N) are arranged as CO_2, H_2O, O_2, N_2, CO, H_2, OH, NO, H, and O in the equilibrium mixture. These 10 unknowns require 10 relationships for their solution. If it is assumed that sufficient fuel and air are used so that the total moles equal the total pressure at equilibrium, the moles of each constituent will represent its partial pressure at equilibrium. If A represents the total moles of air supplied per mole of carbon (7.438 for 100 per cent of required air), $0.79A$ = total moles of N_2 supplied per mole of C. Also, 9/8 = total moles of H_2 per mole of C. Thus, the following three relationships exist between C and N_2, H_2 and N_2, and O_2 and N_2, in which both the moles and the partial pressure of each constituent at equilibrium are represented by the bracketed term:

$$\frac{C}{N_2} = \frac{1}{0.79A} = \frac{[CO_2] + [CO]}{[N_2] + 0.5[NO]} \tag{1}$$

$$\frac{H_2}{N_2} = \frac{9/8}{0.79A} = \frac{[H_2O] + [H_2] + 0.5\{[OH] + [H]\}}{[N_2] + 0.5[NO]} \tag{2}$$

$$\frac{O_2}{N_2} = \frac{1}{3.76} = \frac{[CO_2] + [O_2] + 0.5\{[H_2O] + [CO] + [OH] + [NO] + [O]\}}{[N_2] + 0.5[NO]} \tag{3}$$

The fourth relationship is obtained from Dalton's Partial Pressure Law. Thus,

$$[CO_2] + [H_2O] + [O_2] + [N_2] + [CO] + [H_2] + [OH] + [NO] + [H] + [O] = P \tag{4}$$

The remaining six relationships are obtained from the equilibrium relationships (Table XXV, Appendix).

Thus,

$$[CO_2] = \frac{1}{K_{10}} \frac{[CO][H_2O]}{[H_2]} \tag{5}$$

$$[O_2] = K_7 \left\{\frac{[H_2O]}{[H_2]}\right\}^2 \tag{6}$$

$$[H] = \sqrt{K_1[H_2]} \tag{7}$$

$$[O] = \sqrt{K_2[O_2]} \tag{8}$$

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* HERSEY, R. L., J. E. EBERHARDT, and H. C. HOTTEL, Thermodynamic Properties of the Working Fluid in Internal-combustion Engines, *S.A.E. Jour.*, **39**, 409 (1936).

$$[OH] = \sqrt{K_8\frac{[H_2O]^2}{[H_2]}} \tag{9}$$

$$[NO] = \sqrt{K_4[O_2][N_2]} = \sqrt{K_{11}[N_2]}\frac{[H_2O]}{[H_2]} \tag{10}$$

Substituting Eq. (5) in Eq. (1) and solving for [CO],

$$[CO] = \frac{K_{10}[H_2]\{[N_2] + 0.5[NO]\}}{0.79A\{K_{10}[H_2] + [H_2O]\}} \tag{11}$$

Substituting Eqs (7), (9), and (10) into Eq. (2) and solving for $[H_2O]$,

$$[H_2O] = \frac{\frac{9/8}{0.79A}[N_2] - [H_2] - 0.5\sqrt{K_1[H_2]}}{1 + 0.5\sqrt{\frac{K_8}{[H_2]}} - \frac{9/8\sqrt{K_{11}[N_2]}}{1.58A[H_2]}} \tag{12}$$

Since NO appears in small quantities even at high temperatures, the amount of N_2 in the products will be practically the same as in the mixture before the reaction. Hence, the N_2 may be estimated from the total pressure and will vary from $0.70P$ to $0.75P$ for the range of temperatures and air-fuel ratios considered.

Then, at the desired temperature, which fixes the various K values, a value for $[H_2]$ is assumed. The higher the air-fuel ratio, the lower will be this value. Substituting the various values in Eq. (12) determines the $[H_2O]$ This is followed by determinations of [NO] from Eq (10) and [CO] from Eq. (11). Then, values for $[CO_2]$, [OH], $[O_2]$, [H], and [O] can be obtained from Eqs. (5), (9), (6), (7), and (8), respectively The assumed value of $[H_2]$ is checked by substituting the foregoing results in Eq (3), and the computations are repeated with a different value of $[H_2]$ until a check is obtained.

The total pressure of the equilibrium mixture is determined from Eq. (4) Then, the total moles, pressure, and temperature being known, values for V, E, C, H, and S can be determined for the equilibrium mixture.

Example.—Determine values of P, V, E, C, and S at 5000°R for the reaction between C_8H_{18} and the chemically correct amount of air. The total pressure of the equilibrium mixture at this temperature is to be about 30 atm.

Nitrogen will be assumed to be 21.5 moles. Then, the following constants are obtained for 5000°R from Table XXVI, Appendix, and the computations made as indicated above.

$[N_2] = 21.5$ moles

$0.79A = 5.876$

$K_1 = 0.00603$

$K_2 = 0.00276$

$K_7 = 0.00047$

$K_8 = 0.00174$

$K_{10} = 6.547$

$K_{11} = 0.000004$

$\frac{9/8[N_2]}{0.79A} = 4.116$

$\sqrt{K_{11}[N_2]} = 0.00927$

$\frac{9/8\sqrt{K_{11}[N_2]}}{1.58A} = 0.00089$

$[H_2]$	$0.5\sqrt{K_1[H_2]}$	Numerator, Eq. (12)	$0.5\sqrt{\frac{K_8}{[H_2]}}$	$\frac{0.00089}{[H_2]}$	$1 + 0.5\sqrt{\frac{K_8}{[H_2]}}$	Denominator, Eq. (12)	$[H_2O]$, Eq. (12)
0.14	0.014	3.962	0.0558	0.0064	1.0558	1.049	3.777
0.16	0.015	3.941	0.0522	0.0056	1.0522	1.047	3.764
0.18	0.016	3.920	0.0492	0.0049	1.0492	1.044	3.755
$[H_2]$	$\frac{[H_2O]}{[H_2]}$	[NO], Eq. (10)	$[N_2] + 0.5[NO]$	$K_{10}[H_2]$	Numerator, Eq. (11)	$K_{10}[H_2] + [H_2O]$	Denominator, Eq. (11)
0.14	26.979	0.250	21.625	0.917	19.846	4.694	27.582
0.16	23.525	0.218	21.609	1.048	22.646	4.812	28.275
0.18	20.861	0.193	21.597	1.178	25.441	4.933	28.986
$[H_2]$	[CO], Eq. (11)	$\frac{[CO][H_2O]}{[H_2]}$	$[CO_2]$, Eq. (5)	$K_9[H_2O]$	$K_8\frac{[H_2O]^2}{[H_2]}$	[OH], Eq. (9)	$K_1[H_2]$
0.14	0.720	19.425	2.967	0.00657	0.1773	0.421	0.00081
0.16	0.801	18.844	2.878	0.00655	0.1511	0.393	0.00096
0.18	0.878	18.316	2.798	0.00653	0.1362	0.369	0.00108
$[H_2]$	[H], Eq. (7)	$\left\{\frac{[H_2O]}{[H_2]}\right\}^2$	$[O_2]$, Eq. (6)	$K_7[O_2]$	[O], Eq. (8)	Numerator, Eq. (3)	$N_2 \div O_2$, Eq. (3)
0.14	0.029	727.9	0.342	0.000914	0.031	5.909	3.66
0.16	0.031	553.4	0.260	0.000718	0.027	5.739	3.77
0.18	0.033	435.2	0.205	0.000566	0.024	5.613	3.85

Interpolating the results for a N_2/O_2 ratio of 3.76, the ratio for these constituents in air, results in the values listed as follows:

Medium	Quantity, moles	Internal energy		Chemical energy	
		Per mole	Per quantity	Per mole	Per quantity
H_2O. . . .	3.765	39,885	150,167		
H_2. .	0.158	25,819	4,079	103,486	16,351
CO_2.	2.886	51,365	148,239		
CO. . .	0.794	27,907	22,158	121,181	96,218
O_2. .	0.267	29,616	7,907		
H. . .	0.031	13,346	414	144,565	4,482
O.	0.027	13,346	360	105,833	2,857
OH.	0.396	26,319	10,422	62,444	24,728
NO. . . .	0.221	28,570	6,314	38,746	8,563
N_2 . .	21.500	27,589	593,164		
Sum. . .	30.045 moles		943,224 Btu		153,199 Btu

Substituting the moles of the various constituents in Eq. (4) results in $P_4 = 30.05$ atm, which checks the original $[N_2]$ assumption.

Then,
$$V = \frac{MRT}{P} = \frac{30.05 \times 1545 \times 5000}{30.05 \times 14.7 \times 144} = 3649 \text{ ft}^3$$

Values of U and C from Tables XIX, XXIV, and XXV, Appendix, are used for evaluating U and C for the mixture of gases.

The entropy of each constituent is equal to

$$S = \int c_p \frac{T}{T} - R \ln \text{pp} + S_0$$

Values of $\int c_p dT/T$ are obtained from Table XXII, Appendix. Using the partial pressures in atmospheres for evaluating R ln pp is equivalent to assuming that the data in Table XXII are the entropy values for each medium at 1 atm pr. This makes the basis for entropy the same as used for Chart I. Thus, the entropy of the products is evaluated as follows, including the ΔS of reaction to CO_2 and H_2O (Table XXV).

Medium	Moles M and pressure P	$\int c_p \frac{dT}{T}$	$M \int c_p \frac{dT}{T}$	1.986 M	ln M = ln pp	MR ln pp
H_2O	3.765	22.42	84.411	7.477	1.3257	9.912
H_2..	0.158	27.35	4.321	0.314	−1.8452	−0.579
CO_2	2.886	27.98	80.750	5.732	1.0599	6.075
CO	0.794	38.42	30.505	1.577	−0.2307	−0.364
O_2........	0.267	18.49	4.937	0.530	−1.3205	−0.700
H .	0.031	27.09	0.840	0.062	−3.4738	−0.215
O	0.027	24.78	0.669	0.054	−3.6119	−0.195
OH	0.396	26.12	10.344	0.786	−0.9261	−0.728
NO	0.221	21.03	4.648	0.439	−1.5096	−0.663
N_2	21.500	17.54	377.110	42.699	3.0681	131.005
Sum	30.045		598.535			143.548

$$S = \Sigma M \int c_p \frac{dT}{T} - \Sigma MR \ln \text{pp} = 598.535 - 143.548 = 454.987 \text{ Btu/°R}$$

Total $N_2 = N_2 + 0.5NO = 21.5 + 0.11 = 21.61$ moles
Total $O_2 = N_2 \div 3.76 = 21.61 \div 3.76 = 5.75$ moles
Wt of air = 27.36 × 28.97 = 792.6 lb

Dividing all the results by 792.6 lb provides values as follows for a mixture containing 1 lb of air before combustion:

$T = 5000°R$	$U = 1190$ Btu
$P = 30.05$ atm	$C = 193$ Btu
$V = 4.61 \text{ ft}^3$	$U + C = 1383$ Btu
$S = 0.574$ Btu/°R	

These values check those obtained from Chart I, Appendix, at the same pressure and temperature.

The foregoing method may be used to develop combustion charts for other fuels and oxygen or air in various proportions.

Variation of Temperature of Burned Fraction.—Hopkinson* was the first to call attention to an inherent variation in the temperature of the burned fraction in the constant-volume process. The first fraction of the charge to burn (Fig 107) expands and compresses the unburned fractions as indicated by the path from 1 to 2. This displaces the second fraction, to the position 2–5, and when it burns it compresses the first burned fraction from 2 to 6, and the remaining unburned fractions from 5 to 7.

The last fraction of the charge after being compressed to 2 burns and expands along the line 2 3. In the meantime, the first burned fraction has been compressed along its 2 3 line.

Since $(U_1 + C_1)$ is the same for all fractions, the Energy Equations for the first and last fractions are

$$[(U_1 + C_1) - {}_1W_2 + {}_2W_3]_{\text{1st fraction}} = (U_3 + C_3)_{\text{1st fraction}} \quad (4)$$

and

$$[(U_1 + C_1) + {}_1W_2 - {}_2W_3]_{\text{last fraction}} = (U_3 + C_3)_{\text{last fraction}} \quad (5)$$

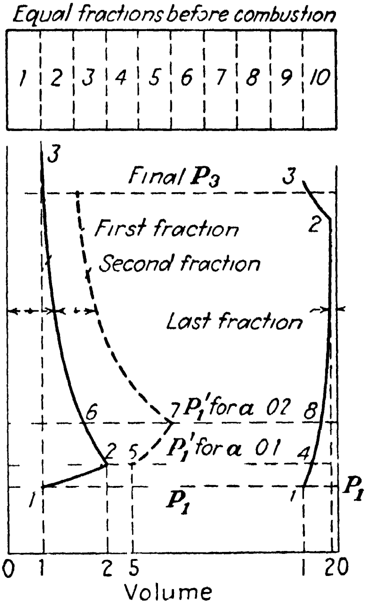

FIG 107.—The combustion process by parts

On the assumption that $V_3 = V_1$ for both fractions,

$${}_2W_3 > {}_1W_2$$

and

$$(U_3 + C_3)_{\text{1st fraction}} > (U_3 + C_3)_{\text{last fraction}} \quad (6)$$

This inequality indicates that T_3 is higher for the first fraction than for the last fraction of the charge to burn. This also indicates that P_3 is higher for the first fraction than for the last fraction if each occupies the same volume. However, the pressure is assumed to be the same, consequently, V_3 for the first fraction must be larger than for the last fraction, which also indicates that T_3 is higher for the first fraction than for the last fraction to burn. Thus, the temperature of the products at the end of the constant-volume combustion process is highest at the point of ignition and lowest at the opposite end of the combustion chamber.

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* CLERK, D., "The Gas Petrol and Oil Engine," p 191, John Wiley & Sons, Inc., New York, 1909.

Example.—Determine the final temperature of the first and last fractions of the charge to burn in a constant-volume combustion of a correct mixture of octane and air. Initial conditions are 100 lb/in² abs and 1000°R. Divide the charge into 10 equal fractions with 1 lb of air in each fraction. Assume no heat loss.

At 1000°R and 100 lb/in² abs Chart H, Appendix, $V = 3.75$ ft³, $U = 100$ Btu, and $C = 1278$ Btu for the correct mixture of octane and air. On Chart I, Appendix, at $V = 3.75$ ft³ and $U + C = 1378$ Btu, $P = 535$ lb/in² abs. This is the pressure attained, assuming that all parts burn simultaneously instead of progressively.

For the burning of first fraction

$$(U + C)_1 = (U + C)_2 + W_{\text{out}}$$

The work out is that of compressing the remaining nine fractions of unburned charge from 1 to 2 (Fig. 107). The solution for condition 2 of the first fraction to burn is made as follows:

Assume P_2	130 lb/in.² abs	140 lb/in.² abs	150 lb/in.² abs
$U_{2\,\text{unb}}$, Chart H	115.8	120.0	123.8*
$9(U_2 - 100) = W_{\text{out}}$	142	180	214
$1378 - W_{\text{out}} = (U + C)_2$	1236	1198	1164
Vol unb, Chart H	3.05	2.90	2.77
$37.5 - 9V_{\text{unb}} = V_{\text{b}}$	10.05	11.40	12.57
V_{b} from P_2 and $(U + C)_2$, Chart I	14.3	13.2	12.2

* These values are readily obtained from a plot of pressure vs. internal energy along a constant S line from the initial conditions.

A plot of the two sets of values for V_{b} vs. P_2 indicates a solution at $P_2 = 148$ lb/in.² abs. At this condition $(U + C)_2 = 1170$ Btu. Compressing the burned fraction isentropically from this condition to the maximum final pressure of 535 lb/in.² abs results in a volume of 4.1 ft³ and a temperature of 5265° R.

To determine the condition of the last tenth to burn, it will be assumed that the first 9 tenths burn simultaneously and compress the last tenth, which then burns and compresses the first 9 tenths to the final pressure. The Energy Equation for the burning of the first 9 tenths is

$$9(U + C)_1 = 9(U + C)_2 + W_{\text{out}}$$

Dividing this energy equation by 9, the solution is made as follows:

Assume P_2	400 lb/in.² abs	500 lb/in.² abs	600 lb/in.² abs
$U_{2\,\text{unb}}$, Chart H	189	206	219
$(U_2 - 100)/9 = W_{\text{out}}/9$	10	12	13
$1378 - W_{\text{out}}/9 = (U + C)_2$	1368	1366	1365
V_{b}, Chart I	5.05	4.05	3.38
$37.5 - 9V_{\text{b}} = V_{\text{unb}}$	−7.95	1.05	7.08
V_{unb}, Chart H	1.27	1.07	0.97

A plot of the two sets of values for V_{unb} vs. P_2 indicates a solution at $P_2 = 503$ lb/in.^{2} abs and $U_2 = 207$ Btu. Compressing the burned 9 tenths isentropically from 503 lb/in.^{2} abs and $U + C = 1366$ to the maximum final pressure of 535 lb/in.^{2} abs results in a $(U + C)$ value per chart quantity of 1390 Btu. The work of compressing the 9 tenths burned is $9(1390 - 1366) = 216$ Btu. Then, the Energy Equation for the last tenth for the burning process is

$$(U + C)_2 - W_{\text{out}} = (U + C)_3$$

or

$$(207 + 1278) - 216 = 1269 \text{ Btu}$$

At 535 lb/in.^{2} abs and $U + C = 1269$ Btu, $V = 3.62$ ft^3 and $T = 4790$°R. Thus, the first tenth has a final temperature 475 F higher than the last tenth to burn. Actually, the final pressure will be slightly lower than 535 lb/in.^{2} abs, which is based on uniform temperature of the products of combustion, because of the effect of temperature variation on specific heats and dissociation.

Effect of Volume Change during Combustion.—Movement of the piston during the first part of the combustion process in an internal-combustion engine decreases the volume and consequently results in a faster pressure rise than would occur with constant-volume combustion (Fig. 108). After top center the movement of the piston reduces the rate of pressure rise until in most cases the combustion process ends with the pressure decreasing.

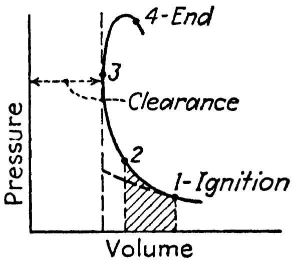

FIG. 108.—Analysis of part of the actual combustion process in an engine.

The Energy Equation for the combustion process from the point of ignition to any point 2 (Fig. 108) is

$$(U_1 + C_1) + {}_1W_2 = (U_2 + C_2) + Q_{\text{out}} \tag{7}$$

$(U_1 + C_1)$ is known from the conditions at ignition, ${}_1W_2$ can be obtained from the work area on the P-V diagram if the process is reversible, and Q_{out} may be estimated, all of which provides a solution for $(U_2 + C_2)$ and for the fraction burned.

Example.—The correct mixture of octane and air is inducted into an engine. The clearance gases amount to one-ninth of the weight of the charge inducted. The conditions at ignition are 90 lb/in.^{2} abs and 1000°R. Combustion proceeds and the piston moves until the pressure is 180 lb/in.^{2} abs and the volume is eight-tenths of the volume at ignition. Determine the amount of charge burned, assuming an adiabatic process.

Assume that the total charge in the cylinder contained originally 1 lb of air. Then, from Chart H, Appendix, the volume at point 1 (Fig. 108) is 4.2 ft^3.

Then,

$$V_2 = 0.8V_1 = 0.8 \times 4.2 = 3.4 \text{ ft}^3$$

$$\int_1^2 P\,dV = 19 \text{ Btu, work in, from area on Fig. 108}$$

$$U_1 + C_1 = 100 + 0.9 \times 1278 = 1250 \text{ Btu (Chart H, Appendix)}$$

Then, $$U_2 + C_2 = 1250 + 19 = 1269 \text{ Btu}$$

Assume that a represents the fraction of the total charge that has been burned up to point 2. Then, at P_2 and S_1 (Chart H, Appendix),

$$U_2 \text{ for the unburned fraction} = (1 - a)140 \text{ Btu}$$
$$V_2 \text{ for the unburned fraction} = (1 - a)2.5 \text{ ft}^3$$
$$C_2 \text{ for the unburned fraction} = (1 - a)(0.9 \times 1278)$$
$$(U_2 + C_2)_{\text{unb}} = (1 - a)1290 \text{ Btu}$$

For the burned fraction,

Assume T_b at point 2	4200	4400	4600
V_{burned} at P_2 and T_b .	9.7a	10.0a	10.4a
$V_2 = 3.4 \text{ ft}^3 = V_b + (1 - a)2.5 \text{ ft}^3$	2.5+7.2a	2.5 + 7.5a	2.5 + 7.9a
a. . .	0.125	0.120	0.114
$(U_2 + C_2)_b$ at P_2 and T_b (Chart I)	1022a	1112a	1210a
or	128	133	138
$(U_2 + C_2)_{\text{unb}} = (1 - a)1290$.	1129	1135	1143
$U_2 + C_2$	1257	1268	1281

Plotting the values of $U_2 + C_2$ against T_b indicates a solution for $U_2 + C_2$ at 1269 Btu at $T_b = 4410°R$ and $a = 0.120$

EXERCISES

1. *a.* Write the reaction equation for H_2 with 30 per cent excess air.

b. Determine the air required and the products in pounds and in cubic feet per pound and per cubic foot of fuel. Volumes of products are measured at 14.7 lb/in.^{2} abs and 250 F. H_2 and air are supplied at 14.7 lb/in.^{2} abs and 60 F.

Ans. 39.4 lb air, 9 lb H_2O, 2.4 lb O_2, and 29 lb N_2, 516 ft^3 air, and 252 ft^3 H_2O, all per pound of H_2

2. The same as Exercise 1 except for CO instead of H_2.

3. *a.* Determine the dew-point temperature for the H_2O produced in the H_2-air reaction for the chemically correct amount of air. Total pressure of the products is 14.7 lb/in.^{2} abs. *Ans.* 163 F.

b. Do the same for CH_4.

c. Do the same for C_8H_{18}.

4. *a.* Determine the percentage of CO_2 obtained by an Orsat analysis of the products of combustion of C with the chemically correct amount of air. *Ans.* 21.0 per cent

b. Do the same for CH_4.

c. Do the same for C_8H_{18}.

d. Do the same for C_2H_6O. *Ans.* 15.1 per cent.

5. *a.* Determine the heat value at constant volume of 1 mole of H_2. The initial mixture temperature is 100 F.

b. Determine the heat value per cubic feet of H_2 at a pressure of 14.7 lb/in.^{2} abs and a temperature of 100 F. *Ans.* 301 Btu.

6. The heat value of gaseous ethyl alcohol at constant pressure and at 77 F is reported as 606,204 Btu/mole. The latent heat of the fuel at 77 F is 18,216 Btu/mole.

a. Determine the chemical energy for the $C_2H_5OH + 3O_2$ reaction.

b. Determine the constant-volume heat value for liquid ethyl alcohol at 90 F.
Ans. 550,555 Btu; 587,354 Btu.

7. A house-heating boiler uses $C_{12}H_{26}$ for fuel. The products of combustion leave the boiler at a temperature of 440 F. The air and fuel flow to the oil burner at a temperature of 60 F, the fuel being liquid. The electric motor supplies 0.1 hp-hr to the oil pump and blower per 2 lb of fuel supplied. The boiler pressure is 20 lb/in.^{2} abs and water at a temperature of 170 F is supplied to the boiler. Assuming a loss of 3 per cent of the chemical energy by heat transfer to the surrounding air, determine the amount of saturated water vapor supplied by the boiler per pound of fuel burned.

8. Determine the constant-volume complete-combustion temperature of H_2 with the chemically correct amount of air, the mixture temperature being 520°R, and the total pressure before combustion being 100 lb/in.^{2} abs. *Ans.* 5485°R.

9. Determine the pressure after combustion for Exercise 8. *Ans.* 898 lb/in.^{2} abs.

10. Solve Exercise 8 for constant-pressure combustion. Determine the volume after combustion per mole of H_2. *Ans.* 4550°R.

11. Determine the constant-volume temperature of combustion for the H_2-air reaction considering chemical equilibrium. Initial conditions are 100 lb/in.^{2} abs and 520°R.

a. Use the chemically correct amount of air. *Ans.* $y = 0.93$; $T = 5040°R$.

b. Use 50 per cent of the chemically correct amount of air.

c. Use 150 per cent of the chemically correct amount of air.

12. Gaseous H_2 and O_2 in the chemically correct ratio and at a temperature of 140 F flow slowly into a combustion chamber at such a rate that the resulting pressure is 500 lb/in.^{2} abs and the temperature is 4000°R, combustion with chemical equilibrium occurring in the chamber. The gases escape from the chamber through a nozzle in which the pressure drops to 14.7 lb/in.^{2} abs in a reversible adiabatic process. Determine the heat loss during combustion and the jet thrust per pound of H_2O escaping per second from the nozzle.

13. Solve Exercise 12, assuming complete combustion and evaluating the flow from the combustion chamber to the atmosphere in two steps: (*a*) from combustion temperature to upper limit of Mollier diagram for H_2O, (*b*) from the upper limit of the Mollier diagram for H_2O to the final pressure of 14.7 lb/in.^{2} abs. Compare the result with that of Exercise 12

14. One pound of air and the chemically correct amount of C_8H_{18} at a total pressure of 100 lb/in.^{2} abs react at constant pressure. Determine the conditions at the end of combustion. Use Chart I in the Appendix.

15. The products of reaction of 1 lb of air and the chemically correct amount of C_8H_{18} are at a temperature of 5000°R and a pressure of 500 lb/in.^{2} abs. Expansion occurs and the volume is increased to six times the original volume. Assuming that the path followed is described by the relation $PV^{1.4} = \text{const}$, determine the work done and the heat transfer for the process.

16. H_2O liquid at 210 F is pumped into a boiler and leaves at a pressure of 300 lb/in.^{2} abs and a temperature of 500 F. The fuel supplied is coal which has the following analysis by weight: moisture, 0.147; ash, 0.073; S, 0.011; H_2, 0.043; C, 0.635; and O_2, 0.091. The heating value of the coal is 9700 Btu/lb. Assume complete combustion occurs with 20 per cent excess air which is supplied at 100 F. The gases leave the boiler at a temperature of 440 F. c_p of SO_2 gas is 11 Btu/mole. Radiation and loss in ash amount to 7 per cent of the heating value of the fuel. Determine the pounds of H_2O supplied the boiler per pound of coal fired.

CHAPTER X

INTERNAL-COMBUSTION ENGINE AND GAS-TURBINE PROCESSES

ENGINE PROCESSES

Classification of Processes.—The two principal engine processes are classified by the method employed for the ignition of the charge, *i.e.*, *spark* or *compression* ignition.

Spark-ignition engines induct (Fig. 109) or, if supercharged, have pumped into the cylinders a combustible mixture of air and fuel. The mixture (including clearance gases) is compressed in the cylinder and ignited when the piston is approaching top-center position. In some cases the fuel is sprayed directly into the cylinder while the air is being inducted. These engines are termed fuel-injection—spark-ignition engines. With both methods of fuel introduction, combustion of the mixture occurs as the piston approaches and recedes from the top-center position. The pressures resulting from combustion make possible an appreciable work effect on the piston of the engine during the expansion stroke. The exhaust valve opens near the end of the expansion stroke, and the pressure in the cylinder drops rapidly to the exhaust pressure as products of com-

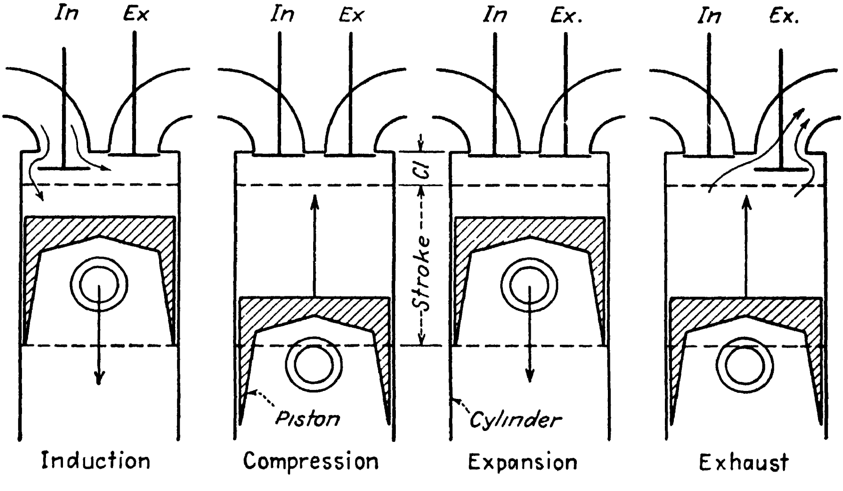

FIG. 109.—The four-stroke internal-combustion engine process.

bustion are released from the cylnder. More of the products are exhausted during the exhaust stroke of the piston, but some remain in the clearance space and mix with the combustible mixture inducted during the following stroke of the piston.

Compression-ignition engines usually induct air only and compress the air and the small amount of clearance gases to a pressure and temperature sufficiently high to ignite the mixture resulting from the spraying of fuel into the cylinder as the piston approaches top center. The combustion process starts as a result of the effect of the temperature attained during compression. The remaining parts of the process are the same as for the spark-ignition engine.

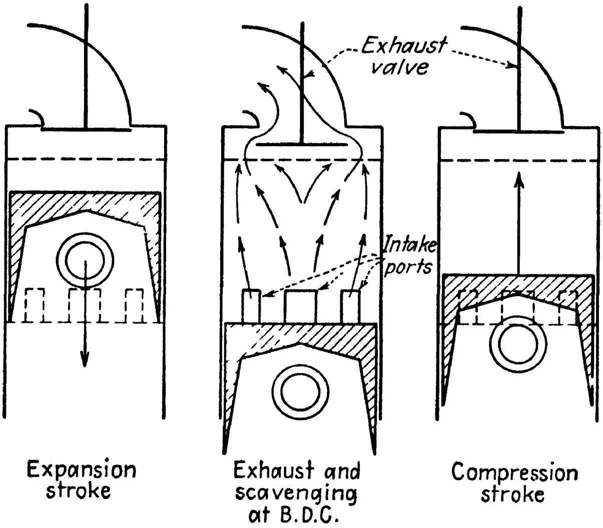

FIG. 110.—The two-stroke internal-combustion engine process.

The four strokes of the piston—induction, compression, expansion, and exhaust, for both of the foregoing cases—complete a cycle for the engine mechanism, which has resulted in the term *four-stroke* engine or cycle. These engines have one power stroke per cylinder per two revolutions of the engine crankshaft. In other engines the exhaust and induction strokes are eliminated by having these processes occur while the piston is near the bottom-center position (Fig. 110). In such cases the exhaust valves are opened or the exhaust ports are uncovered as the piston approaches the bottom-center position. This is followed by the opening of intake ports or valves through which the combustible mixture or air flows into the cylinder. The cylinder and ports are designed so that the entering air or mixture will drive most of the exhaust products out of the cylinder and provide it with a fresh charge of air or combustible mixture. Thus, only two strokes of the piston are required and this has resulted in the term *two-stroke* engine or cycle.

While the mechanism of the internal-combustion engine undergoes a cyclic process, the mediums involved are not returned to the original condition of mixture and clearance products, and consequently do not undergo a cyclic process. Hence the method set forth in the chapter on Cycles *cannot* be applied to the actual internal-combustion engine process.

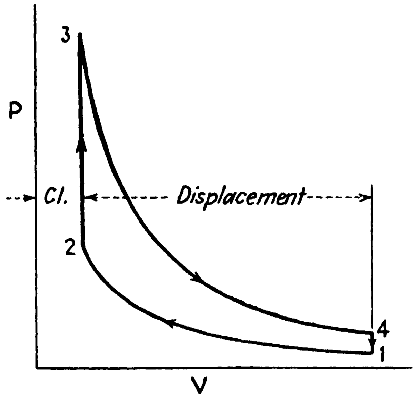

FIG. 111.—*P-V* diagram of Air-Standard Otto Cycle.

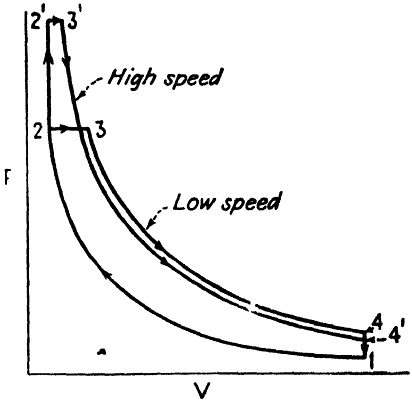

FIG. 112.—*P-V* diagrams of Air-Standard Diesel or compression-ignition cycles.

In the ideal analysis the spark-ignition engine is usually assumed to have constant-volume combustion at top-center piston position, and this engine has long been termed the *Otto* engine (Fig. 111). Constant-pressure combustion is usually assumed for the ideal analysis of low-speed compression-ignition engines, and these have long been termed *Diesel* engines (Fig. 112). However, high-speed compression-ignition engines are usually assumed to have a combustion process which in the ideal case, may be assumed to approach a constant-volume process to a limiting (maximum desirable) pressure, and a constant-pressure process for the remainder of the combustion process (Fig. 112). Actually, the *P-V* diagram of the combustion process for the high-speed compression-ignition engine is very similar to the actual diagram for the spark-ignition engine (see Fig. 116).

Air-Standard Analysis.—The most elementary analysis of the internal-combustion engine process is based on the assumption that the medium is air only. The medium is compressed adiabatically and reversibly. Heat is added to the air while the volume remains constant or while the piston moves, depending on the type of process desired. Adiabatic reversible expansion begins at the end of the heating process and extends, usually, to the original volume. Heat is then rejected until the medium is returned to the original condition. Thus, in the Air-Standard Cycle, the usual cyclic analysis may be employed. The analysis is simplified further by the assumption of constant specific heats.

For the Otto-engine process (Fig. 111),

$$Q_{\text{in}} = Mc_V(T_3 - T_2) \tag{1}$$

$$Q_{\text{out}} = Mc_V(T_4 - T_1) \tag{2}$$

Then for a cycle,

$$\text{Net } W = Q_{\text{in}} - Q_{\text{out}} \tag{3}$$

$$\text{Thermal eff} = \frac{\text{net work}}{Q_{\text{in}}} = 1 - \frac{T_4 - T_1}{T_3 - T_2} \tag{4}$$

$$= 1 - \frac{T_1}{T_2}\left(\frac{T_4/T_1 - 1}{T_3/T_2 - 1}\right) \tag{5}$$

For the adiabatic reversible expansion and compression processes,

$$\frac{T_4}{T_3} = \left(\frac{V_3}{V_4}\right)^{k-1} = \left(\frac{V_2}{V_1}\right)^{k-1} = \frac{T_1}{T_2} \quad \text{(see page 73)} \tag{6}$$

and, consequently,

$$\frac{T_4}{T_1} = \frac{T_3}{T_2} \tag{7}$$

Also, (V_1/V_2) is the compression ratio, r. Hence Eq. (5) becomes

$$\text{Thermal eff} = 1 - r^{1-k} \tag{8}$$

Example.—Determine the air-standard efficiency for the Otto-engine process with a compression ratio of 6 to 1.

$$\text{Thermal eff} = 1 - 6^{-0.4} = 0.512$$

The air-standard analysis of the Diesel-engine process for slow-speed engines (Fig. 112) is based on constant-pressure heating and results in

$$\text{Thermal eff} = 1 - \frac{1}{k}\frac{(T_4 - T_1)}{(T_3 - T_2)} \tag{9}$$

This expression may be manipulated into a form involving r, r_{cp}, and r_{exp}, where r_{cp} is the volume expansion ratio for constant-pressure combustion and r_{exp} is the adiabatic reversible volume expansion ratio. Obviously,

$$r = r_{\text{cp}} \times r_{\text{exp}} \tag{10}$$

and the lower the value for r_{cp} the higher the value for r_{exp}, and the higher the thermal efficiency will be for a given compression ratio r.

The air-standard analysis for the Diesel-engine process for high-speed engines (Fig. 112) is based on constant-volume heating to the maximum desirable pressure, and constant-pressure heating from this point to the end of the combustion process. This analysis results in

$$\text{Thermal eff} = 1 - \frac{T_4 - T_1}{(T_2' - T_2) + k(T_3 - T_2')} \tag{11}$$

This expression may also be manipulated into a form involving r, r_{cp}, and r_{exp}. Also, the higher the value for r_{exp} the higher the efficiency will be for a given compression ratio r.

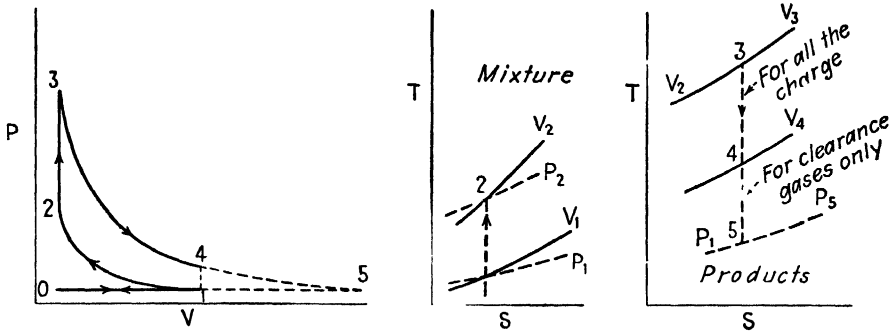

FIG. 113.—*P-V* and *T-S* diagrams for the ideal Otto-engine process with the actual mixture.

Actual Process Analysis.—Goodenough and Baker* improved the internal-combustion engine analysis by considering actual mixtures, clearance gases, variable specific heats, and chemical equilibrium. The computations are quite involved but are much simplified when charts such as those of Hottel† are available for the actual mixture.

All processes are assumed to be adiabatic, and only the combustion and release processes are irreversible. Such analyses result in thermal efficiencies about 30 per cent lower than obtained with the air-standard analysis, and these efficiencies can be reconciled with actual practice when the deviations between assumed and actual conditions are considered.

Ideal Otto or Spark-ignition Engine Analysis.—The charge in the cylinder at the end of the induction stroke of a four-stroke engine (0 to 1, Fig. 113) consists of a clearance-gas weight fraction, f, and the fresh-mixture weight fraction, $1 - f$. The pressure during the induction stroke is assumed to be the same as intake-manifold pressure. It is necessary to assume the clearance-gas fraction f which varies with compression ratio r and intake-manifold conditions, and also to assume the temperature of the charge at the end of the induction stroke.

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* GOODENOUGH, G. A., and J. B. BAKER, *Univ. Ill. Eng. Exp. Sta. Bull.* 160 (1927).

† *Ibid.*, p. 205.

The pressure and temperature at the end of the induction stroke are the conditions for the beginning of the compression stroke, which process is solved by the use of the chart for the air-fuel ratio of the inducted charge. Then,

$$W_{\text{comp}} = U_2 - U_1 \tag{1}$$

Example.—Liquid octane and the chemically correct amount of air at 60 F flow through a carburetor into the intake manifold and are inducted into an engine cylinder. The compression ratio is 6:1. The pressure is 14.7 lb/in.^{2} at the end of the suction stroke in the ideal normally aspirated case at sea level. It will be assumed that f, the clearance-gas fraction, is 0.036, that T_1 of the charge is 100 F, and that the fuel is completely vaporized at the beginning of the compression stroke. Determine the conditions at the end of the adiabatic reversible compression stroke and the work of compression.

From Chart H, Appendix, at $P_1 = 14.7$ and $T_1 = 560°\text{R}$, $S_1 = 0.071$, $U_1 = 9$ Btu, and $V_1 = 14.3$ ft^3.

$$V_2 = V_1/r = 14.3/6 = 2.38 \text{ ft}^3$$

At $V_2 = 2.38$ ft^3 and $S_1 = S_2 = 0.071$, $U_2 = 108$ Btu and $P_2 = 165$ lb/in.^{2}

Then, $$W_{\text{comp}} = U_2 - U_1 = 108 - 9 = 99 \text{ Btu}$$

The Energy Equation for the combustion process is

$$(1 - f)C + U_2 = U_3 + C_3 \tag{2}$$

Knowing V_2 and $U_3 + C_3$, the conditions at the end of constant-volume combustion can be determined from the combustion chart for the given air-fuel ratio.

Example.—Determine the conditions at the end of constant-volume combustion for the data in the previous example. For the given air-fuel mixture C is 1278 Btu.

Then, $$U_3 + C_3 = (1 - 0.036)1278 + 108 = 1340 \text{ Btu}$$

On Chart I, Appendix, at $V_2 = 2.38$ ft^3 and $U_3 + C_3 = 1340$ Btu,

$$S_3 = 0.5165 \quad \text{and} \quad P_3 = 850 \text{ lb/in.}^2$$

The expansion process is adiabatic and reversible. Hence, $S_3 = S_4$ (Fig. 113). The expansion process ends at $V_4 = V_1$, at which point P_4 and $U_4 + C_4$ can be determined. The work of expansion is

$$W_{\text{exp}} = (U_3 + C_3) - (U_4 + C_4) \tag{3}$$

At the end of the expansion stroke the exhaust valve opens, the combustion products escape from the cylinder, and the pressure decreases theoretically to atmospheric. The gases remaining in the cylinder theoretically have expanded adiabatically and reversibly to the atmospheric or exhaust pressure. Consequently, the *specific* conditions of the combustion products that will remain in the clearance space at the end of the exhaust stroke are determined at S_3 and at atmospheric (or exhaust) pressure. These data provide a means for checking the assumed value of f, the clearance-gas fraction. Thus, V_5 is the specific volume of the clearance gases per chart quantity, and V_2 is the volume of these gases retained in the clearance space. Consequently,

$$f = V_2/V_5 \tag{4}$$

Example.—Determine the conditions at the end of the adiabatic reversible expansion stroke for the data given in the preceding example. Also check the value of f previously assumed.

At $S_3 = 0.5165$ and $V_4 = V_1 = 14.3\text{ ft}^3$,

$$U_4 + C_4 = 770\text{ Btu} \qquad \text{and} \qquad P_4 = 103\text{ lb/in.}^2$$

Continuing the expansion on Chart I to the atmospheric pressure of 14 7 lb/in.^{2} results in $V_5 = 66\text{ ft}^3$ and $U_5 + C_5 = 440$ Btu at the same entropy. Then

$$f = V_2/V_5 = 2.38/66 = 0.0361$$

which checks the assumed f of 0.036.

Usually f will not be checked on the first trial and data at point 4 need not be determined until a check of f and T_1 has been accomplished. The value determined for f on the first trial should be used for the assumed value for the second trial.

The piston pushes all but the clearance gases out of the cylinder during the exhaust stroke. This process is theoretically reversible and adiabatic and does not change the condition of the gases that remain in the clearance space. The work done by the piston on the gases during the exhaust process is

$$W_{\text{exh}} = P_{\text{atm}}(V_1 - V_2) \tag{5}$$

The induction process in the normally aspirated engine occurs at atmospheric pressure in the ideal case.

The work done on the piston during the induction process is

$$W_{\text{ind}} = P_{\text{atm}}(V_1 - V_2) \tag{6}$$

Thus, the work of the exhaust process equals the work of the induction process, and both may be eliminated in this case.

The air and fuel flow into the carburetor and then through the intake manifold into the engine (Fig. 114) where the incoming fresh charge mixes with the clearance gases and does work on the piston. The Energy Equation for the induction process is

$$(1 - f)[H_{\text{air}} + (F/A)\, H_{C_8H_{18}}]_a + fU_5 = P_{\text{atm}}(V_1 - V_2) + U_1 \tag{7}$$

in which F/A is the fuel-air ratio and subscript a indicates the atmospheric* condition. The U_1 obtained from this relation must check the value for the assumed T_1 or a new value must be assumed and the solution repeated.

Example.—Analyze the induction process for the data given in the preceding examples. The H for 1 lb of air at 60 F for which the charts are constructed is $1033 \div 28.97 = 35.7$ Btu (Table XIX, Appendix).

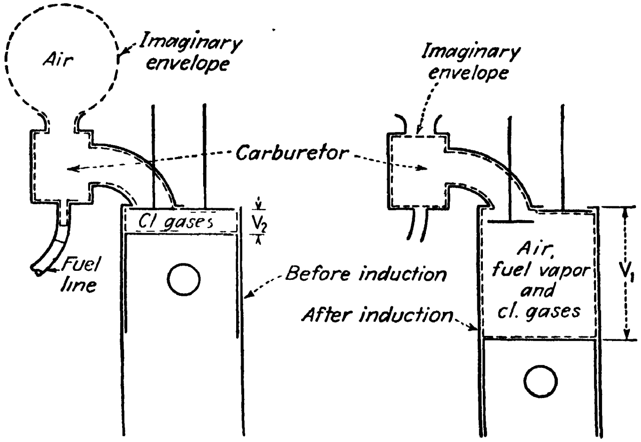

FIG. 114.—Induction process for the spark-ignition internal-combustion engine. (The mixture in the carburetor and connection to the cylinder is assumed to remain constant from cycle to cycle and consequently may be disregarded in the analysis.)

The fuel-air ratio is based on the stoichiometric relation between octane and air. Thus, from the molal relation in the reaction equation and the molecular weights,

$$\frac{F}{A} = \frac{1 \times 114}{59.5 \times 28.97} = 0.066$$

The latent heat of octane, H_{fg}, is 17,730 Btu/mole at 77 F (Table XXIV, Appendix). The H for gaseous octane at 77 F is 1740 Btu/mole (Table XX, Appendix). Thus the H of liquid octane at 77 F is $1740 - 17{,}730 = -15{,}990$ Btu/mole or -140 Btu/lb. The specific heat of liquid gasoline is about 0.5 Btu/lb. Cooling the liquid octane from 77 to 60 F decreases its enthalpy to -148.5 Btu.

Substituting these and other known data in Eq. (7) results in

$$(1 - 0.036)(35.7 - 0.066 \times 148.5) + 0.036 \times 440$$
$$= 14.7 \times 144(14.3 - 2.38)/778 + U_1$$

or

$$U_1 = 9.0$$

which checks the value for U_1 corresponding to the assumed T_1.

The net work of the series of processes is

$$\text{Net } W = W_{\text{exp}} - W_{\text{comp}} + W_{\text{ind}} - W_{\text{exh}} \tag{8}$$

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* This might also be the condition in the air manifold leading to the carburetor.

In the ideal normally aspirated engine the last two work items are equal.

The mean effective pressure is

$$\text{mep} = \frac{\text{net work}}{\text{displacement}} \tag{9}$$

The specific fuel consumption (sfc) is the pounds of fuel per horsepower-hour of work. One horsepower-hour is equivalent to 2544 Btu of work. Consequently,

$$\frac{\text{Fuel consumption}}{\text{Btu net work}} \times \frac{2544\ \text{Btu}}{\text{hp-hr}} = \frac{\text{fuel consumption}}{\text{hp-hr}} \tag{10}$$

$$\text{Thermal eff} = \frac{\text{net work}}{Q_{\text{supplied}}} \tag{11}$$

The combustion-engine process is not a cycle, and no heat is supplied. Consequently, it is customary to charge the engine with the constant-pressure heat of combustion of the fuel supplied.

Example.—Determine the mean effective pressure and the thermal efficiency of the combustion-engine process illustrated in the preceding examples.

$$\text{mep} = \frac{\text{net work}}{V_1 - V_2} = \frac{[(1340 - 770) - 99]\,778}{(14 - 2.38)144} = 218\ \text{lb/in.}^2$$

$$\text{sfc} = \frac{(1 - 0.036)0.066}{471} \times \frac{2544}{1} = 0.344\ \text{lb/hp-hr}$$

The constant-pressure heat of combustion of liquid octane at 77 F (Table XXIV, Appendix) is

$$\frac{2{,}368{,}089 - 17{,}730}{114} \times 0.066 = 1362\ \text{Btu/lb}$$

$$\text{Thermal eff} = \frac{\text{net work}}{Q_P} = \frac{471}{(1 - 0.036)1362} = 0.358$$

This is about 30 per cent less than was obtained by the air-standard analysis (page 218).

A similar analysis may be made assuming that sufficient heat is supplied the air-fuel mixture in the intake manifold to result in the vaporization of the fuel. The conditions in the intake manifold for the ideal case at sea level would be atmospheric pressure and the minimum temperature required for complete vaporization of the fuel.*

Ideal Diesel or Compression-ignition Engine Analysis.—The four-stroke Diesel engine inducts air which mixes with the clearance gases. This gaseous mixture is then compressed adiabatically and reversibly to a temperature sufficiently high* to ignite the mixture resulting from the injection of the fuel. The Energy Equation for the compression process is

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* See Lichty, L. C., "Internal Combustion Engines," McGraw-Hill Book Company, Inc., New York, 1939.

$$[(1 - f)U_{\text{air}} + fU_{\text{cl}}]_1 + W_{\text{comp}} = [(1 - f)U_{\text{air}} + fU_{\text{cl}}]_2 \tag{1}$$

Values for T_1 and f are assumed as in the Otto-engine analysis. The condition at the end of compression is indicated by the entropy of the mixture of gases since $S_1 = S_2$ for the process.

The injection of the liquid fuel and the combustion process may be analyzed as one process. Assuming adiabatic constant-pressure combustion, the Energy Equation for this process is

$$[M(U + C) + \Delta PV]_{\text{fuel}} + [(1 - f)U_{\text{air}} + fU_{\text{cl}}]_2 = P_3(V_3 - V_2) + (U + C)_3 \tag{2}$$

in which M is the fuel quantity in moles per $(1 - f)$ lb of air inducted,
ΔP is the ideal pressure difference in the injection pump†,
V is the specific volume of liquid fuel,
and subscripts 2 and 3 indicate the conditions at the end of compression and combustion, respectively.

Octane may be used as the fuel since the H/C ratio is nearly that of fuel oil. Also this assumption permits the use of the combustion Chart I, Appendix, for the case of no excess air. The final pressure is the same as the compression pressure. Assumption of the final temperature (T_3) indicates the value of $(U + C)_3$ and V_3 on the combustion Chart I, the correct assumption satisfying Eq. (2).

The expansion and release processes may be solved in the usual manner with Chart I, thus determining the work, clearance fraction f, and its energy content. The determined f must check the assumed f or the computation repeated with another assumption of the value of f.

The Energy Equation for the induction process is

$$[(1 - f)H_{\text{air}}]_{\text{man}} + fU_5 = P_1(V_1 - V_2) + [(1 - f)U_{\text{air}} + fU_{\text{cl}}]_1 \tag{3}$$

The condition of the air in the intake manifold in the ideal case may be assumed to be 60 F and atmospheric pressure. The energy content of the air and clearance gases at the end of the induction stroke must check that for the assumed T_1.

The net work of the ideal normally aspirated Diesel-engine process is the difference between the sum of the works of combustion and expansion and the work of compression.

Ideal Limited-pressure Diesel-engine Process.—The analysis for this process is the same as that for the previous process, with the exception that P_3 is limited to some pressure that may range between 700 and 1,500 lb/in.^{2}

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* Compression ratios may range from 8:1 to 20:1.

† The injection pressure may vary from about 2,000 to 20,000 lb/in.^{2}, while the fuel supply pressure is not much above atmospheric. Hence, the injection pressure may be used for ΔP without introducing appreciable error.

Effect of Compression Ratio.—The effect of compression of the charge in the internal-combustion engine is to increase the temperature and pressure before combustion occurs. The higher the compression ratio, the higher will be the temperature at which combustion starts, and the higher will be the temperature of the products after combustion. Carnot's principle indicates that the availability of the energy in the products after combustion will be higher with the higher temperature accompanying higher compression ratio. However, the increase in maximum temperature after combustion is not as much as might be anticipated because of the effect of increase in specific heats and dissociation at high temperatures. Also, in actual practice higher combustion temperatures increase the heat-transfer loss. Consequently, it appears that the higher combustion temperatures are not primarily responsible for the increase in work and efficiency when the compression ratio is increased.

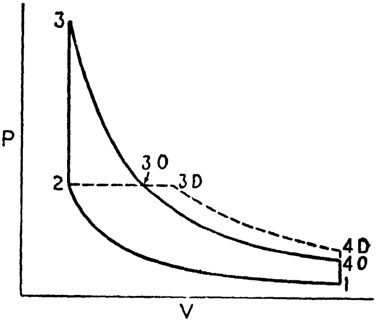

Fig. 115.—Comparison of Air-Standard Otto and constant-pressure Diesel processes with the same compression ratios

The expansion ratio in the ideal Otto engine is the same as the compression ratio. An increase in expansion ratio increases appreciably the amount of work obtainable in an engine. Thus, higher compression ratios, while increasing the availability of the energy liberated because of higher maximum temperatures, make possible the transformation of more of the energy liberated into work because of higher expansion ratios.

Energy liberated during the expansion stroke is liberated at a piston position which permits a lower expansion ratio than if liberated at top-center piston position. Consequently, the ideal Otto engine with constant-volume combustion is more efficient than the Diesel engine for the same compression ratio, since in the Diesel engine the energy is liberated at a piston position indicating a lower mean expansion ratio.

The thermal efficiency of an ideal adiabatic engine process (Figs. 111 to 113) is

$$\text{Thermal eff} = \frac{\text{net work}}{Q_P} = \frac{(U + C)_1 - (U + C)_4}{Q_P} \tag{4}$$

Comparing the air-standard Otto-engine process with the air-standard constant-pressure Diesel-engine process, both processes have the same charge energy at 2, namely $(U + C)_2$ (Fig. 115).

At point $3D$ for the Diesel-engine process, the charge energy will be

$$(U + C)_{3D} = (U + C)_2 - {}_2W_{3D} \tag{5}$$

At point $3O$ for the Otto-engine process the charge energy will be

$$(U + C)_{3O} = (U + C)_2 - {}_3W_{3O} \tag{6}$$

Obviously, if points $3D$ and $3O$ were identical, ${}_3W_{3O}$ would be greater than ${}_2W_{3D}$ and $(U + C)_{3O}$ would be less than $(U + C)_{3D}$. Hence point $3O$ must be at a lower volume than $3D$ as indicated. Then, $(U + C)_{4D}$ is higher than $(U + C)_{4O}$ and from Eq. (4) the Otto-engine process is inherently more efficient than the Diesel-engine process for the same compression ratio.

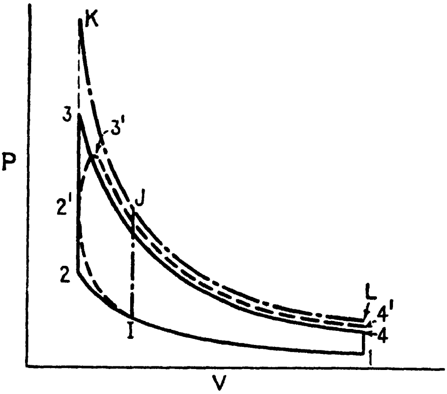

FIG. 116.—*P-V* diagrams for illustrating the effect of variations in combustion on the efficiency of the Otto-engine process

The same method may be used to prove that increasing the compression ratio increases the thermal efficiency.

Ignition and Injection Timing.—The combustion process requires an appreciable amount of time. Hence, it is necessary to ignite the charge (or begin fuel injection in the Diesel engine) before the end of the compression stroke in order to obtain the highest mean expansion ratio for the products of combustion. Combustion of fuel before and after the end of the compression stroke occurs at piston positions where only lower than ideal cycle expansion ratios are possible. If all the fuel burned instantly at the point of ignition (*I*, Fig. 116) the path followed after ignition would be *IJKJL*. If all the fuel burned at the point of ignition but during the expansion stroke, the path followed would be *I2IJL*, the net result being the same amount of work, which is obviously less than that for the ideal or actual processes since the energy value at *L* is greater than that at 4′ or 4. The actual process follows the path $12'3'4'$, and point 4′ indicates less work than that for the ideal process.

The optimum spark advance (or injection advance) results in the maximum work which is obviously less than the work of the ideal process.

Fuel-air Ratio.—Maximum work is obtained from mixtures containing more than the chemically correct amount of fuel because of the possibility of complete consumption of the oxygen in the charge. Similarly, minimum specific fuel consumption is obtained from mixtures containing more than the chemically correct amount of oxygen because of the possibility of complete consumption of the fuel in the charge.* Charts for rich and lean mixtures have been prepared and facilitate the analysis of engine processes with these mixtures.

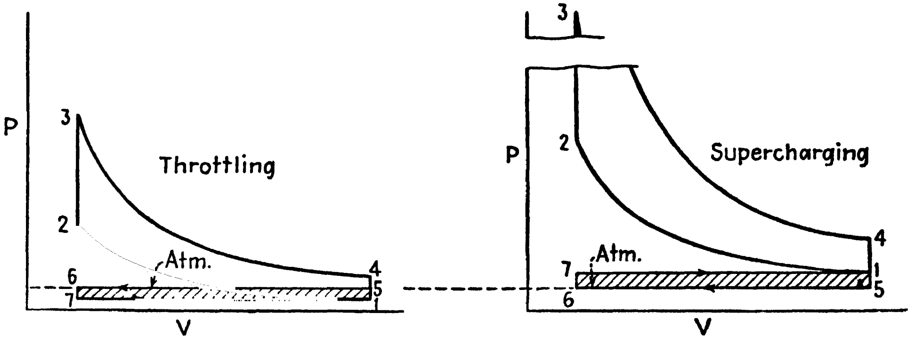

Fig. 117.—P-V diagrams of ideal throttling and supercharging Otto-engine processes.

Throttling.—Most spark-ignition engines are controlled as to speed and output by throttling the charge inducted into the engine cylinder. The Energy Equation for the ideal induction process is the same as Eq. (7), (page 221), P_1 being lower than atmospheric. At the beginning of the process some of the clearance gases flow into the manifold as the intake valve opens,† thereby reducing the cylinder pressure to that of the induction stroke which is assumed to be constant at P_1. The compression, combustion, and expansion processes are analyzed as before. The net work of the entire engine process is the algebraic summation of the various work effects. Thus, from Fig. 117,

$$\text{Net work} = ({}_3W_4 - {}_1W_2) - ({}_5W_6 - {}_7W_1) \tag{1}$$

The work area 1-2-3-4-1 for the ideal throttled case is smaller than the same area for the ideal unthrottled case but the ideal efficiency based on this area is not changed appreciably. Consequently, the pumping-work area 5-6-7-1-5 caused by throttling reduces the ideal thermal efficiency. Also, throttling increases the clearance-gas fraction which dilutes the smaller amount of charge inducted and results in slower burning. This necessitates earlier spark advance for optimum results and also reduces the thermal efficiency.

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* *Ibid.*, p. 223.

† Unless intake-valve opening is appreciably later than top-center piston position.

Theoretically, more dilution with clearance gases results in a lower maximum temperature, and this tends to increase the efficiency because of the effect of lower mean specific heats. However, more dilution necessitates the use of richer mixtures to obtain regular ignition of the charge, and the foregoing effect is more than offset by the additional fuel requirement.

Supercharging.—The output of combustion engines is increased by supercharging, which is merely forcing more air or mixture* into the engine than could be normally aspirated. Superchargers are usually steady-flow compressors which may be of the positive displacement type or of the centrifugal or axial type. The method for analyzing these processes is illustrated in the chapter on Processes.

Assuming that liquid fuel is sprayed into the air entering a supercharger, the Energy Equation for an adiabatic supercharger process is

$$[H_{\text{air}} + (F/A)H_{\text{liq fuel}}]_{\text{atm}} + W_{\text{in}} = [H_{\text{air}} + (F/A)H_{\text{vap fuel}}]_{\text{man}} \qquad (1)$$

In the ideal frictionless case the entropy of the mixture remains constant. The initial atmospheric condition of the air and fuel, and the discharge or manifold pressure (the total pressure), are usually known. Hence, the solution of Eq. (1) is made by assuming the fuel to be vaporized at discharge conditions, and also assuming various values for T_2 until S_2 equals S_1.†

The Energy Equation for the induction process for the engine cylinder is

$$(1 - f)\,[H_{\text{air}} + (F/A)H_{\text{vapor}}]_{\text{man}} + fU_{\text{cl}} = U_1 + P_1V_{\text{disp}} \qquad (2)$$

Using 1 lb of air and F/A ratio of 0.066 permits the use of the compression and combustion charts (Appendix) for the remainder of the process. Some of the work of supercharging is reclaimed in the engine as indicated by the work area 6-7-1-5-6 (Fig. 117), which is added to the ideal work area 1-2-3-4-1 to obtain the net work of the engine process alone. Subtracting the work of supercharging results in the net work of the engine-supercharger combination.

The analysis of the engine-supercharger process may be simplified by assuming that sufficient heat is added to the fuel-air mixture during or before induction into the supercharger to result in complete vaporization of the fuel before compression in the supercharger. In this case the mixture chart, H, Appendix, may also be used for the supercharger process. However, this assumption results in higher mixture specific volume and less supercharging for the same discharge pressure compared to the case of liquid fuel entering the supercharger.

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* With fuel injection the fuel may be injected into the engine manifold during the induction or compression process.

† This problem is complicated if condition 2 is not such that the fuel is completely vaporized or superheated.

The use of a centrifugal or axial steady-flow supercharger introduces an inherently irreversible process,* with an accompanying increase in entropy of the medium during the process. The work of supercharging is appreciably more than that required for the adiabatic reversible process attaining the same discharge pressure. The ratio, y, between the adiabatic reversible process and the adiabatic irreversible process is about 0.70 and is commonly known as the adiabatic efficiency of the supercharger. Thus, referring to Fig. 67,

$$y = \frac{H_5 - H_1}{H_3 - H_1} \tag{3}$$

Usually, air only is considered in determining the adiabatic efficiency, although the same method may be applied to a mixture undergoing the supercharger process.

Detonation-limited Operation.—The increase in compression ratio that results in an increase in output and thermal efficiency, and the increase in supercharge that results principally in an increase in output, are limited by the phenomenon of detonation of the last part of the charge to burn. The phenomenon of detonation depends on such items as fuel characteristics, combustion-chamber design, air-fuel ratio, compression ratio, and operating conditions. Incipient detonation for a given engine, fuel, fuel-air ratio, and operating speed, is indicated by the end-mixture condition.† This is the temperature and density of the last part of the charge to burn. Thus, continuing the compression process from 1 to 2 (Fig. 113) up to the maximum pressure attained during the combustion process indicates the end-mixture condition. Various combinations of manifold pressure and temperature, for a given air-fuel ratio, will result in incipient detonation for a given engine and set of operating conditions. The corresponding end-mixture conditions for incipient detonation are determined as indicated in the foregoing. A plot of the end density vs.

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* This is also the case with the Root type of blower which permits air from the discharge line to flow into the blower and compress the inducted air to the discharge pressure before the rotors discharge the air.

† ROTHROCK, A. M., and A. E. BIERMAN, *Nat. Advisory Comm. Aeronau.*, *Rept.* 655, 1939.

end temperature indicates the maximum end-mixture conditions above which detonation will occur for the given engine and operating conditions.

The analysis for detonation-limited operation is the same as previously set forth. For any chosen compression ratio a manifold pressure is assumed and the engine process analyzed. After the assumed f and T_1 (or U_1) have been checked, the end-mixture condition is determined. If the end-mixture condition is above the incipient detonation end-mixture curve, a lower manifold mixture is assumed and the computations repeated until the end-mixture conditions check those for incipient detonation.

Obviously, low compression ratios will permit high manifold-mixture pressures (high supercharge) while high compression ratios will require throttling to prevent incipient detonation.

TURBINE PROCESSES

Elementary Gas Turbine.—The elementary gas turbine requires a compressor (Fig. 118) which inducts air from the atmosphere and compresses it to the desired discharge pressure. The discharged air flows to the burner into which the desired amount of fuel is injected and burned at compressor discharge pressure in the ideal case Low fuel-air ratios are used since the maximum temperature permitted by turbine materials is about 1500 F.

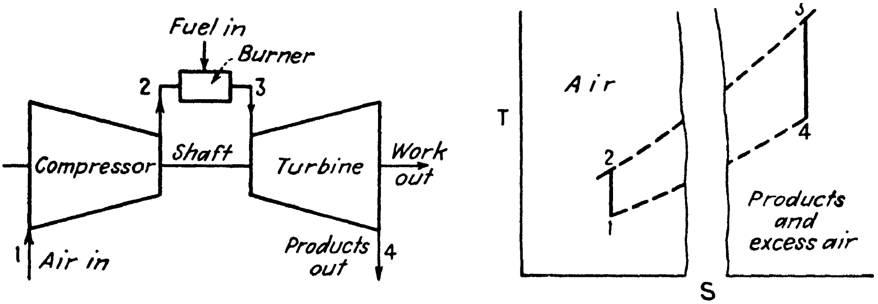

FIG. 118.—Apparatus and T-S diagrams for an elementary ideal gas-turbine process.

The products of combustion, which include a large percentage of excess air, expand in the turbine, do work on the rotor, and are exhausted at atmospheric pressure. The work obtained from the ideal turbine, assuming negligible kinetic energy effects, is the difference of the enthalpies of the mediums before and after the process. Thus,

$$W_{\text{turb}} = (H_3 - H_4)_S \tag{1}$$

The work required by the ideal compressor, assuming negligible kinetic energy effects, is

$$W_{\text{comp}} = (H_2 - H_1)_S \tag{2}$$

The Energy Equation for the combustion process is

$$M_F C_{F+O_2} + M_F H_F + (H_2)_a = (M_a H_a)_3 + (M_p H_p)_3 \tag{3}$$

in which subscripts a, F, O_2, p, and S indicate air, fuel, oxygen, products of combustion and entropy, respectively.

The efficiency of the process is

$$\text{Eff} = \frac{(H_3 - H_4)_S - (H_2 - H_1)_S}{M_F Q_P} \tag{4}$$

in which Q_P is the heat value of the fuel.

The fuel-air ratio by weight is

$$F/A = (M_F m_F)/(M_a m_a) \tag{5}$$

in which m is the molecular weight.

The T-S diagram for the entire process is divided into two parts: one for the air flowing through the compressor, and the other for the mixture of products of combustion and excess air flowing through the turbine. Both the reaction and mixing processes influence the entropy of the mixture that flows through the turbine so that the pressure lines on the two parts of the T-S diagram would not coincide with each other if the same entropy scale were used for both. However, they have been placed in this position to illustrate the process with air only as the medium, having heat transferred into the medium instead of the reaction between part of the air and the injected fuel.

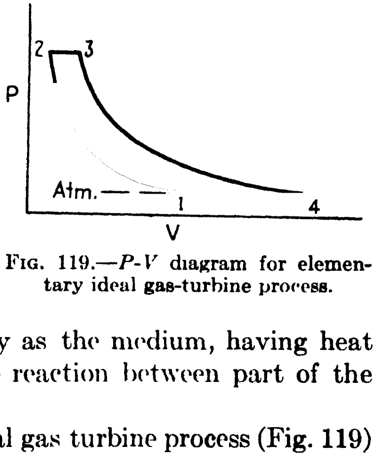

FIG. 119.—P-V diagram for elementary ideal gas-turbine process.

The pressure-volume diagram for the ideal gas turbine process (Fig. 119) consists of two isentropics (1 to 2 and 3 to 4) connected by the constant-pressure combustion process (2 to 3) at the high-pressure ends, the other ends being located at atmospheric pressure. If it is assumed that the heat is transferred to the air from an outside source of heat instead of by reaction between fuel and part of the air, it would be possible to cool the air from turbine exhaust condition to compressor inlet condition (4 to 1), and thus make the gas-turbine process a cycle.* This cycle has been known for years as the *Brayton cycle.*

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* This cycle has been proposed with the system sufficiently charged with air or some inert medium so that the lowest pressure of the cycle would be appreciably above atmospheric. This would reduce the size of apparatus required for a given output. In this case regeneration (Fig. 120) is used and a precooler is inserted at the compressor entrance to reduce the work of compression.

The air-standard analysis of this Brayton cycle results in the same expression for the thermal efficiency of the cycle as was obtained for the Otto cycle, *i.e.*,

$$\text{Thermal eff} = 1 - r^{1-k} \tag{6}$$

where r is the volumetric compression ratio (V_1/V_2).

Regeneration of Turbine Exhaust Energy.—The gases are exhausted from the turbine usually at a temperature appreciably higher than the temperature of the air leaving the compressor. This permits the use of a heat exchanger or regenerator (Fig. 120) to transfer some of the energy from the exhaust gases to the compressed air before entering the burner. This reduces the amount of fuel required to attain the maximum permissible turbine inlet temperature and consequently increases the thermal efficiency of the unit.

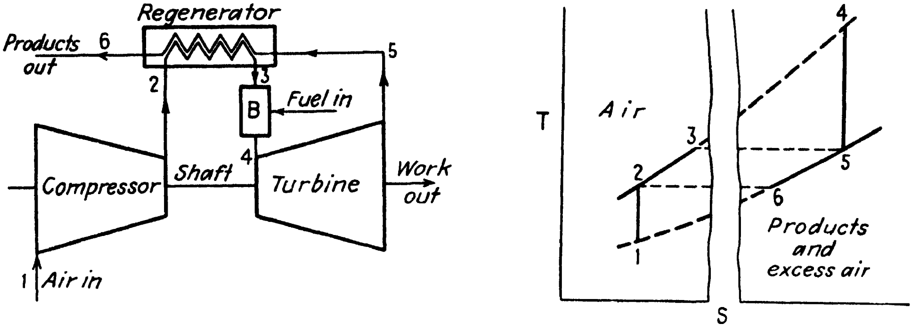

FIG. 120.—Apparatus and T-S diagrams for an elementary ideal gas-turbine process with 100 per cent regeneration.

The maximum amount of heat that can be transferred in the counterflow regenerator occurs when the temperature of the air is heated to turbine exhaust temperature. In this case the temperature of the exhaust gases leaving the regenerator will be slightly above the compressor discharge temperature, because of the difference in specific heats of the turbine exhaust gases and air for the same temperature range. This case is designated as 100 per cent regeneration. If 50 per cent of the maximum possible amount of heat is added to the compressed air, the process is designated as 50 per cent regeneration.

The amount of heat transferred in the regenerator, assuming negligible *KE* effects and no heat loss to the surrounding atmosphere, is

$$Q = M_{\text{air}}\,(H_3 - H_2) = M_{\text{prod}}\,(H_5 - H_6) \tag{7}$$

from which T_6 may be determined.

Two-stage Compression, Intercooling, and Regeneration.—The work of compression may be reduced by two-stage compression and intercooling (Fig. 121). Usually cooling fluids at a temperature lower than the atmosphere are not available and 100 per cent or perfect intercooling is ordinarily the maximum attainable. It has been shown in the chapter on Cycles that the reduction in work of compression with perfect intercooling is a maximum when the receiver pressure is

$$P_r = \sqrt{P_1 \times P_4} \tag{8}$$

It was also shown that the adiabatic reversible compression process results in the same temperature rise in both stages and that the pressure ratio in both stages is the same.

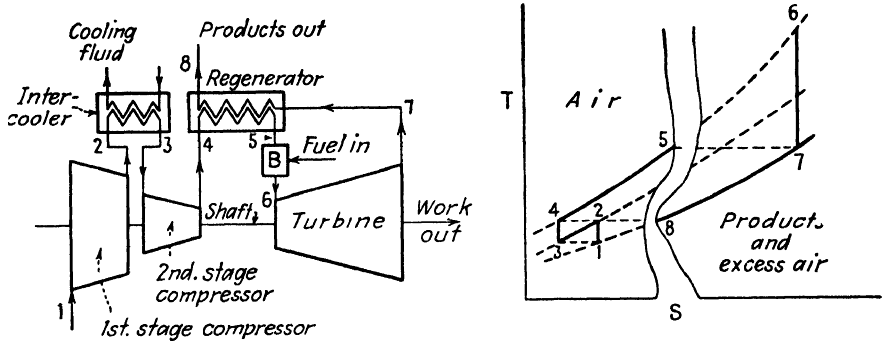

FIG. 121.—Apparatus and *T-S* diagram for an ideal gas-turbine process with two-stage compression and perfect intercooling and 100 per cent regeneration.

Although two-stage compression with intercooling increases the net work obtained from the entire process, more energy must be supplied the air discharged from the compressor to increase its temperature to turbine inlet conditions. Inspection of the *T-S* diagram in Fig. 121 indicates that the introduction of intercooling necessitates the use of regeneration or the thermal efficiency would be less than that of the elementary process with single-stage compression.

Example.—A gas turbine operates with a pressure ratio of 4 to 1. The compression process is divided into two stages with best receiver pressure and perfect intercooling. Atmospheric air at 60 F is inducted into the first stage of the compressor; 100 per cent regeneration is assumed. Determine the net ideal work and ideal thermal efficiency, using air as the medium in the turbine and assuming a turbine inlet temperature of 2000°R.

$$\text{Best receiver pressure} = \sqrt{4 \times 1} = 2 \text{ atm}$$

$$\int c_P \frac{dT}{T} \text{ at 60 F} + R \ln 2/1 = 0 + 1.377 = 1.377 \quad \text{(Table XXII)}$$

This is the $\int c_P \frac{dT}{T}$ at P_1 and T_2 (Fig. 121). From Table XXII, $T_2 = 634°\text{R}$.

In a similar manner T at S_1 and P_4 is determined to be 771°R, and T_7 is determined to be 1406°R. Using data from Table XIX,

$$\text{Work of compression} = (H_2 - H_1) + (H_4 - H_3) = 2(1826 - 1033) = 1586 \text{ Btu/mole of air}$$

$$\text{Work of expansion} = H_6 - H_7 = 12{,}059 - 7413 = 4646 \text{ Btu/mole of air}$$

$$\text{Net work} = 4646 - 1586 = 3060 \text{ Btu/mole of air}$$

$$\text{Heat supplied} = H_6 - H_5 = 12{,}059 - 7413 = 4646 \text{ Btu}$$

$$\text{Ideal thermal eff} = 3060/4646 = 0.66$$

Without Intercooling or Regeneration

$$\text{Ideal thermal eff} = \frac{4646 - (2787 - 1033)}{12{,}059 - 2787} = \frac{2892}{9272} = 0.312$$

With Intercooling Only

$$\text{Ideal thermal eff} = \frac{3060}{12{,}059 - 1826} = \frac{3060}{10{,}233} = 0.297$$

All these thermal efficiencies are much higher than can be attained in practice because of compressor and turbine efficiencies that have been assumed to be 100 per cent and also because of the assumption of no pressure drop through the intercooler, burner, and regenerator.

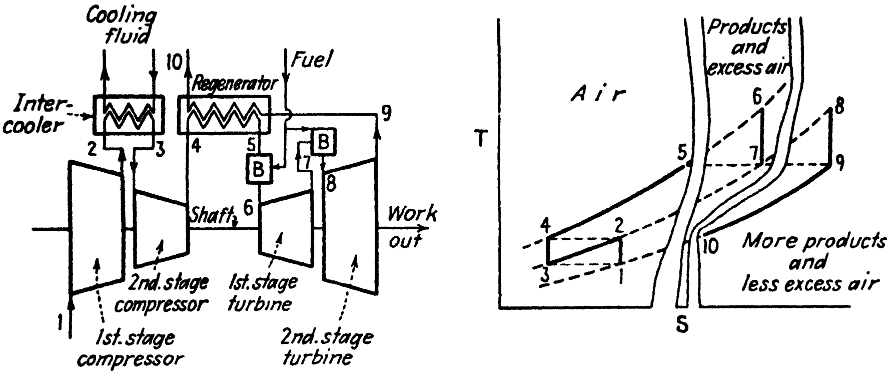

FIG. 122.—Apparatus and T-S diagrams for an ideal gas-turbine process with two-stage compression and perfect intercooling, two-stage expansion with reheating, and 100 per cent regeneration.

Two-stage Compression and Expansion, Intercooling, Two-stage Combustion and Regeneration.—The work of the turbine may be increased appreciably by expanding the gases in two stages and reheating the gases between the two stages up to the maximum possible turbine inlet temperature (Fig. 122). The reaction equation for the second-stage combustion process is

$$M_F'C_{F+O_2} + (M_aH_a)_7 + (M_pH_p)_7 = (M_a'H_a)_8 + (M_p'H_p)_8 \qquad (9)$$

in which the prime indicates the quantity for the second-stage combustion process and subscripts F, a, and p indicate fuel, air, and products, respectively.

Considerably more energy of the turbine exhaust gases is regenerated in this case than in one-stage expansion, since the exhaust temperature is appreciably higher than for single-stage expansion.

High-pressure Gas-turbine Processes.—All the foregoing gas-turbine processes are operated usually between a low pressure of atmospheric and a high pressure in the range of 4 to 8 atm. The closed system mentioned in the footnote on page 231 is operated at higher pressures. Another system operates at high pressures by utilizing an auxiliary turbine to drive a compressor which pumps air at its discharge pressure into a burner in the main system. Fuel is injected into the air and burned to heat the medium in the main system. Some of the total medium passing through the burner is bled from the system to operate the auxiliary turbine and compressor.

Friction and Kinetic-energy Effects.—The actual processes in the compressor and turbine are not reversible isentropics as assumed for the ideal cases, but are friction processes which result in entropy increases. These effects are introduced by efficiencies. Thus,

$$\text{Compressor eff} = \frac{\text{ideal } \Delta H}{\text{actual } \Delta H} \tag{1}$$

and

$$\text{Turbine eff} = \frac{\text{actual } \Delta H}{\text{ideal } \Delta H} \tag{2}$$

Both of these efficiencies are usually in the range of 0.70 to 0.85, the upper limit indicating excellent performance.

Pressure drop occurs in the burner and heat exchangers because of friction and momentum effects. See Chap. XI.

Turbines have leaving losses because of high exit gas velocities. See Chap. XI.

Combustion Chart for Low Fuel-air Ratios.—The maximum possible performance of gas-turbine processes using air only, or air and fuel, is readily computed by the use of Chart J, Appendix. This chart is constructed for the quantity of air and fuel that results in 1 mole of products including the excess air. This quantity of fuel-air mixture which varies with fuel-air ratio is termed the *chart quantity.*

Values of $\int c_p dT/T$, $H + C$ for the fuel-air mixture, and H of the products have been plotted in Chart J for various excess air values. The fuel supplied is assumed to be liquid dodecane at 60 F. The $\int c_p dT/T$ lines are used in the customary manner to determine the conditions at the end of the compression and expansion processes.

Example.—Solve Exercise 15 at the end of this chapter for a pressure ratio of 10 to 1 and a maximum temperature of 2000°R, by using Chart J (*a*) assuming the medium to be air only, (*b*) using the actual fuel-air mixture and products therefrom.

Air-cycle Analysis

At 60 F (Chart J), the $\int c_P dT/T$ is 0, which is the value for S_1. Then,

$$S_2 \text{ at } P_1 \text{ and } T_2 = S_1 + R\ln(P_2/P_1) = 0 + 4.57 = 4.57$$

The intersection of the S_2 entropy line and the all-air line indicates 993°R for T_2. Also, the intersection of the T_1 and T_2 lines and the all-air enthalpy line indicates 1033 and 4340 Btu/mole of air for H_1 and H_2, respectively.

At 2000°R, H_3 is 12,070 Btu, and $\int c_P dT/T$ or S_3 is 9.87 Btu/°R per mole of air. Then,

$$S_4 \text{ at } P_2 \text{ and } T_4 = S_3 - R\ln(P_2/P_1) = 9.87 - 4.57 = 5.30$$

At this value for S_4, T_4 is 1103°R and H_4 is 5120 Btu/mole of air.

$$\begin{aligned} \text{Then,}\quad & \text{Work of expansion} = H_3 - H_4 = 12{,}070 - 5120 = 6950 \text{ Btu} \\ \text{and}\quad & \text{Work of compression} = H_2 - H_1 = 4340 - 1033 = \underline{3307} \text{ Btu} \\ & \text{Net work} = 3643 \text{ Btu/mole of air} \end{aligned}$$

The Q supplied $= H_3 - H_2 = 12{,}070 - 4340 = 7730$ Btu, and

$$\text{Eff} = \frac{\text{net work}}{Q_{in}} = \frac{3643}{7730} = 0.471$$

This efficiency is about 2 per cent lower and the work value of 3643 Btu/mole of air is about 8 per cent higher than that for the Air-Standard Brayton Cycle for the same pressure ratio.

Actual Mixture Analysis

T_2 is 993°R as in the air cycle analysis since only air is compressed. Also $R\ln(P_2/P_1) = 4.57$ as before.

The 2000°R line intersects the 200 per cent excess-air line at an H value of about 12,420 Btu. The intersection of this H line and the 993°R line indicates a first approximation of the excess-air value of about 345 per cent. Again, the intersection of the 2000°R line and the 345 per cent excess-air line occurs at a value of about 12,320 Btu, which indicates, as explained before, an excess-air value of 350 per cent. Thus, this trial-and-error solution for the excess-air value converges very rapidly to a solution.

S_3 at 2000°R and 350 per cent excess air is found to be about 10.07. Hence, S at P_2 and T_4 is 10.07 − 4.57 or 5.50. The intersection of this entropy line and the 350 per cent excess-air line indicates that T_4 is 1118°R. The intersection of the T_4 line and the 350 per cent excess-air line indicates an H_4 value of 5360 Btu.

H_2 and H_1 are the same as for the air-cycle analysis, but the moles of air per mole of products is 0.984, as indicated at the upper end of excess-air lines in the lower part of Chart J.

$$\begin{aligned} \text{Then,}\quad & \text{Work of expansion} = H_3 - H_4 = 12{,}320 - 5360 = 6960 \text{ Btu} \\ \text{and}\quad & \text{Work of compression} = M(H_2 - H_1) = 0.984(4340 - 1033) = \underline{3254} \text{ Btu} \\ & \text{Net work} = 3706 \text{ Btu} \end{aligned}$$

The high heating value for the amount of fuel used is 8650 Btu as indicated by the intersection of the 350 per cent excess-air line and the high heat value line. Then,

$$\text{Eff} = \frac{3706}{8650} = 0.428$$

This efficiency is about 11 per cent lower than that of the Air-Standard Brayton Cycle for the same pressure ratio and about 10 per cent lower than computed for the air-cycle analysis.

The fuel-air ratio for the chemically correct mixture of dodecane, or $C_nH_{2.167n}$ is 0.068. Then for 350 per cent excess air

$$F/A = 0.068/4.50 = 0.0151$$

Since 0.984 mole of air is required per mole of products, the net work per mole of air supplied is 3706/0.984, or 3766 Btu. This is about 12 per cent more work than obtained with the Air-Standard Brayton Cycle and about 3 per cent more work than obtained in the actual air-cycle analysis, all for the same pressure ratio.

EXERCISES

Most can be accomplished in many of these exercises by assigning each student a different value for the principal variable such as compression ratio, and plotting the results of the various parts of the solutions.

Internal-combustion Engines

One of exercises 7, 8, 9, 12, and 13 should prove sufficient practice in this work, since all are long and are solved in a similar manner.

1. Compute the air-standard thermal efficiency for the Otto-engine process with various compression ratios, and plot efficiency vs. compression ratio r.

2. Compute the mean effective pressures for each compression ratio used in Exercise 1 and plot the mean effective pressure vs. r. Assume that the heat supplied is equal to that liberated by the reaction between octane and the chemically correct amount of air.

3. Transform the expression for the thermal efficiency of the constant-pressure Diesel-engine process into an expression containing the various expansion ratios.

4. Compute the air-standard thermal efficiency and mean effective pressure for the constant-pressure Diesel-engine process with various compression rates, and plot efficiency and mean effective pressure vs. r. Use both 50 and 100 per cent of maximum heat supplied as indicated in Exercise 2.

5. The same as Exercise 3 but for the limited-pressure Diesel-engine process.

6. Compute the air-standard thermal efficiency and mean effective pressure for the limited-pressure Diesel-engine process with various compression ratios and plot the efficiency and mean effective pressure vs. r. Use the maximum heat supplied as indicated in Exercise 2, and solve for 25, 50, and 75 per cent heat supply at constant volume. Use 1000 lb/in.^{2} abs as the limiting pressure.

7. Compute the ideal thermal efficiency, mean effective pressure, and specific fuel consumption for the Otto-engine process with various compression ratios and plot efficiency vs. r. Liquid octane and the chemically correct amount of air at 60 F are flowing to the carburetor. Compare the results with those of Exercises 1 and 2.

8. Compute the ideal thermal efficiency, mean effective pressure, and specific fuel consumption for the Diesel-engine process with constant-pressure combustion for various compression ratios and plot efficiency vs. r. Liquid octane at 60 F is supplied the injection pump. The temperature of the air supply is 60 F. Injection pressure is 5000 lb/in.^{2} Compare the results with those of Exercise 4.

9. Solve Exercise 8 for a limited-combustion pressure of 1,000 lb/in.^{2} Compare the results with those of Exercise 6.

10. Prove that the Diesel limited-pressure engine process is less efficient than the Otto-engine process for the same compression ratio.

11. Assuming that the charge and its conditions are the same in both cases at the beginning of compression, prove that increasing the compression ratio increases the thermal efficiency of the ideal engine processes.

12. Compute the ideal thermal efficiency, mean effective pressure, and specific fuel consumption for the throttled Otto-engine process for various induction pressures ranging from 14 7 lb/in.^{2} down to that induction pressure which results in net work equal to zero. Air and the chemically correct amount of liquid fuel are supplied the carburetor at 60 F and 14.7 lb/in.^{2} Compression ratio is 6:1. Assume that the Mixture Chart H, Appendix, is correct for all cases. Plot thermal efficiency vs. P_1.

13. Assuming that air and a chemically correct amount of liquid octane at 60 F are supplied an ideal supercharger of an engine, determine the thermal efficiency, mean effective pressure, and specific fuel consumption for supercharger pressure ratios of 2:1 and 3:1. Engine compression ratio is 6:1.

Gas Turbines

14. Prove that the air-standard efficiency of the Brayton cycle is the same as for the Otto cycle.

15. Determine the net work and efficiency for the elementary gas-turbine process for pressure ratios from 2:1 to 10:1, and plot the results against pressure ratios. Atmospheric air is at 60 F and 14.7 lb/in.^{2} Use the energy and entropy tables for air, neglecting the effect of the products during the turbine process. Determine the quantity of fuel required from the actual reaction process. Use turbine inlet temperatures of 1500, 2000, and 2500°R

16. Solve Exercise 15 with 100 per cent regeneration.

17. Solve Exercise 15 with two stages of compression with optimum pressure ratios and perfect intercooling.

18. Solve Exercise 17 with 100 per cent regeneration.

19. Solve Exercise 18 with two stages of expansion and reheating to first-stage inlet temperature.

20. Solve Exercise 18 using a turbine inlet temperature of 2000°R only, with a compressor efficiency of 0.75 and a turbine efficiency of 0.80. Compare the result with that of Exercise 18 for the same turbine inlet temperature.

21. Solve Exercise 20 for a pressure ratio of 6:1 only, with a pressure drop of 0.5 lb/in.^{2} in all heat exchangers. Compare the result with that of Exercise 20.

22. Solve Exercise 15 for a pressure ratio of 6:1 only, and a turbine inlet temperature of 2000°R only, using data for the actual mediums for the turbine process, and compare the result with that of Exercise 15 for the same conditions.

23. Solve Exercise 16 for a pressure ratio of 10:1 and a maximum temperature of 2000°R, making use of Chart J.

CHAPTER XI

THE FLOW OF FLUIDS

GENERAL

Energy, Mass, Momentum, and Entropy Relations.—The flow of a fluid from one position to another is caused either by a difference in pressure or by a difference in elevation between the two positions. An elevation or pressure difference accelerates the fluid acted upon from a state of rest, or given condition of velocity, to the maximum velocity that can be obtained with the given conditions. A state of steady flow is eventually attained with a given pressure difference, under which condition the velocity, pressure, etc., at any given position remain constant. The steady-flow Energy Equation may be applied, omitting those forms of energy not involved in the given process. Thus,

$$PE_1 + KE_1 + U_1 + P_1V_1 + W_{in} + Q_{in} = PE_2 + KE_2 + \cdots + Q_{out} \quad (1)$$

The Energy Equation may be applied also to nonsteady-flow processes as already indicated.

Steady flow implies that the quantity of fluid flowing past any position in a unit of time is the same. Thus, for positions 1, 2, 3, etc.,

$$M = M_1 = M_2 = M = \cdots = M_n \quad (2)$$

The fluid is assumed to fill the flow channel and, since the velocity is constant at any position in the line of flow, it follows that

$$M = A_1w_1\ V_1 = A_2w_2\ V_2, \text{ etc.} \quad (3)$$

where A is the area of cross section of flow channel taken perpendicularly to the direction of flow,

w is the velocity of flow,*

and V is the specific volume of the fluid, all at the given position.

This equation is commonly known as the *continuity* or *mass equation.*

When several fluids, a and b, enter a process and leave as a mixture the mass equation would be

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* The velocity of flow in a pipe line or duct varies theoretically from zero at the pipe surface to a maximum at the center of the pipe. Consequently, the mean velocity at any given section should be used. Also, the mean kinetic energy should be evaluated for cases in which the velocities are of such magnitude that an appreciable error is introduced in using the mean velocity for its evaluation.

$$(M_a + M_b)_1 = A_2 w_2 / V_2 \tag{4}$$

The mixing of fluids usually occurs with differences in the initial velocities but with a common final velocity. If the velocities are appreciable, the momentum equation should be applied. In this case, the difference between the final and initial momentums is the applied force. Thus,

$$(P_1 - P_2)A = (M_a + M_b)w_2 - (M_a w_a + M_b w_b)_1 \tag{5}$$

in which M is the mass rate of flow
P is the pressure per unit area at the subscript position,
and A is the area of both sections at positions 1 and 2.

All the foregoing relations are based on the principles of Conservation of Energy, Mass, and Momentum.

The Second Law of Thermodynamics indicates that for adiabatic processes

$$S_2 \geqq S_1$$

The entropy of the medium remains constant during reversible adiabatic processes, but for all *actual adiabatic processes the entropy of the medium usually increases* during the process.

Reynolds Number.—Flow may be either laminar or turbulent. Laminar flow implies that the various lamina or flow lines do not mix. A small colored stream introduced into a fluid under laminar-flow conditions maintains its identity. Turbulent flow implies the mixing of the various lamina or flow lines with many resulting eddy currents. A small colored stream when introduced into a fluid under turbulent-flow conditions breaks up and colors the entire stream very soon after introduction into the stream.

Reynolds* discovered that the condition of flow is indicated by the dimensionless ratio

$$\text{Reynolds no., } Re = \frac{\text{inertia force}}{\text{viscous force}} = \frac{w^2 l^2 \rho}{\mu w l} = w d\rho/\mu = wd/\nu \tag{6}^\dagger$$

where w = velocity of flow, ft/sec,
d = diameter of the pipe, ft, substituted for the length dimension l,
ρ = density of the fluid, slugs/ft^3, or lb sec^2/ft^4,

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* REYNOLDS, O., The Motion of Water and the Law of Resistance in Parallel Channels, *Trans. Roy. Soc.* (*London*), **A174**, 935 (1883).

† TIETJENS, O. G., "Applied Hydro- and Aeromechanics," p. 6, McGraw-Hill Book Company, Inc., New York, 1934.

DODGE, R. A., and M. J. THOMPSON, "Fluid Mechanics," p. 423, McGraw-Hill Book Company, Inc., New York, 1937.

μ = absolute viscosity, lb sec/ft^2,[*]

and, μ/ρ = kinematic viscosity, ν, ft^2/sec (see Chart K, Appendix).

Turbulent flow occurs usually when the Reynolds number is 2,000 or above. Below this critical value, the flow is usually laminar. However, turbulent flow may occur with a Reynolds number as low as 1,200. See Chart L, Appendix.

Mach Number.—Mach number is a dimensionless criterion for the effect of compressibility in flow processes. It is defined as the ratio between inertia and elastic forces. Thus,

$$\text{Mach no.} = \frac{\text{inertia force}}{\text{elastic force}} = \frac{\rho l^2 w^2}{l^2 E} = \frac{\rho l^2 w^2}{\rho l^2 w_c^2} = \frac{w^2}{w_c^2} \qquad (7)\dagger$$

in which E is the modulus of elasticity, and subscript c indicates the acoustic condition.

However, for practical purposes,

$$\text{Mach no.} = \sqrt{w^2/w_c^2} = w/w_c \qquad (8)$$

Velocities below the speed of sound (*subsonic*) are indicated by Mach numbers less than unity, while in the *supersonic* region the Mach numbers are greater than unity. When the Mach number is less than 0.5, a compressible fluid in a flow process may be treated as incompressible with small error in the determination of the stagnation or total pressure.

Total Temperature and Pressure.—The temperatures and pressures of a flowing medium are the *static* values. A Pitot tube pointing upstream in the moving fluid will indicate the total or stagnation pressure. This is the pressure resulting from the adiabatic-reversible process of stopping the fluid flow. The Energy Equation for this process is

$$H_1 + KE_1 = H_2 \qquad (9)$$

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[*] The absolute viscosity is the force per unit area required to maintain a unit difference in velocity between two parallel surfaces a unit distance apart in the fluid. Thus,

$$\mu = \frac{\text{force}}{\text{area}} \times \frac{\text{dist apart}}{\text{vel diff}} = \frac{F}{A} \times \frac{dl}{dw} = \frac{\text{lb}}{\text{ft}^2} \times \frac{\text{ft}}{\text{ft/sec}} = \text{lb sec/ft}^2$$

In the metric system,

$$\mu = \frac{\text{gm} \times \text{cm/sec}^2}{\text{cm}^2} \times \frac{\text{cm}}{\text{cm/sec}} = \text{gm/(cm sec)} = \text{poises}$$

1 centipoise = 0.01 poise = 2.09×10^{-5} lb sec/ft^2

$$\text{Kinematic viscosity, } \nu, = \frac{\mu}{\rho} = \frac{\text{lb sec/ft}^2}{\text{lb sec}^2/\text{ft}^4} = \text{ft}^2\text{/sec}$$

$$\text{Reynolds number} = \frac{wd\rho}{\mu} = \frac{wd}{\nu} = \frac{\text{(ft/sec)ft}}{\text{ft}^2\text{/sec}} = \text{dimensionless}$$

† DODGE and THOMPSON, *loc. cit.*, p. 431.

The temperatures corresponding to H_1 and H_2 are the *static* and *total* or *stagnation* temperatures, respectively.

Knowing the *static* pressure P_1, the static temperature T_1, and the total temperature T_2, the *total* pressure P_2 can be determined in the usual manner from the relation for the adiabatic-reversible process. Thus, if a gaseous medium,

$$\Delta S = \int c_P \frac{dT}{T} - R \ln \frac{P_2}{P_1} = 0 \tag{10}$$

The Mollier diagram may be used for saturated and superheated vapors.

FLOW THROUGH ORIFICES

Liquids.—The flow of a liquid through an orifice at the bottom of a column of the liquid may be determined by analyzing the process between positions at the top of the column and at the orifice exit (1 and 2, respectively, Fig 123). At both of these positions the pressure and specific volume of the liquid will be the same. The temperature will be constant since the liquid may be assumed to be incompressible, and the process is usually adiabatic. Also, mechanical work is not associated with the process. Thus, the Energy Equation becomes

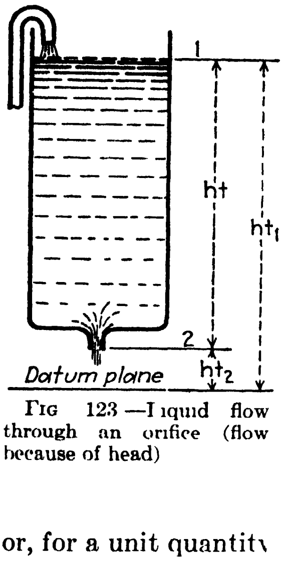

Fig 123—Liquid flow through an orifice (flow because of head)

$$PE_1 + KE_1 = PE_2 + KE_2 \tag{1}$$

or, for a unit quantity of liquid,

$$(w_2{}^2 - w_1{}^2)\ 2g = ht_1 - ht_2 \tag{2}$$

If the area of cross section at position 1 is large compared with the orifice cross section, w_1 will be negligible and

$$u_2 = \sqrt{2g(ht_1 - ht_2)} = \sqrt{2g\,ht} \tag{3}$$

when *ht* represents the height or elevation of section 1 above section 2.

Example.—Determine the theoretical velocity with which liquid H_2O will flow through an orifice subjected to a head of 100 ft The area of the orifice is 1 per cent of the area of the section at the 100-ft elevation

Since the same quantity and volume of liquid H_2O flow through the orifice and the 100-ft head section, the velocities will vary inversely with the section areas Hence referring to Fig 123,

$$w_1 = 0\,01 w_2$$

Obviously w_1^2 is negligible compared to w_2^2, and

$$w_2 = \sqrt{2 \times 32.2 \text{ ft/sec}^2 \times 100 \text{ ft}} = 80.2 \text{ ft/sec}$$

Flow may occur through an orifice in a pipe line or reservoir under pressure. In this case (Fig. 124) the positions 1 and 2, between which the Energy Equation is to be applied, are at the same level so that the *PE* terms are eliminated. Also, *U*, *W*, and *Q* terms are eliminated. However, the pressure varies, and consequently the Energy Equation becomes

$$KE_1 + P_1V_1 = KE_2 + P_2V_2 \qquad (4)$$

or

$$(w_2^2 - w_1^2)/2g = V(P_1 - P_2) \qquad (5)$$

The dimensions of $V(P_1 - P_2)$ are foot-pounds per pound of material. This is equivalent to the potential energy stored in a pound of liquid at the height *ht* (Fig. 124) of the column of liquid indicating the pressure difference between the two chosen positions. Thus, the analyses of flow on a head basis and on a pressure basis are identical.

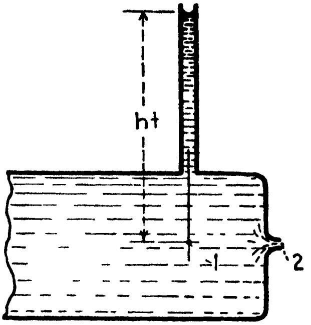

FIG. 124.—Liquid flow through an orifice (flow because of pressure).

Example.—Determine the theoretical quantity of liquid H_2O that will flow from an orifice having an area of 1 in.², the orifice being located in the side of a large reservoir in which the pressure at the orifice level is 58.0 lb/in.² abs.

Obviously w_1 is negligible since the reservoir is large. Thus,

$$w_2^2/2g = V(P_1 - P_2)$$

or

$$w_2 = \sqrt{2 \times 32.2 \times 144(58.0 - 14.7)/62.4}$$

$$= 80.2 \text{ ft/sec}$$

This result is the same as the result of the previous example since the difference in pressure is equivalent to a head of 100 ft.

The quantity discharged per second will be the product of the orifice area in square feet, the velocity in feet per second, and the specific weight of the fluid flowing in pounds per cubic foot. Thus,

$$M = Aw/V = (1/144) \times 80.2 \times 62.4 = 34.8 \text{ lb/sec}$$

Perfect Gases.—The flow of gases through orifices occurs as a result of pressure difference. The expansion process is assumed to be reversible in the ideal case, and consequently there is an appreciable change in *U* and *T*. The temperature change of the gas makes possible some heat transfer between the orifice and the flowing gas. However, this is of negligible amount because of the small surface area and time element so that the process may be assumed to be adiabatic. Thus,

$$KE_1 + U_1 + P_1V_1 = KE_2 + U_2 + P_2V_2 \tag{1}$$

or

$$(w_2^2 - w_1^2)/2g = H_1 - H_2 \tag{2}$$

If w_1 and the variation in specific heat are negligible,

$$w_2 = \sqrt{2gc_P(T_1 - T_2)} \tag{3}$$

since H is a function of the temperature for perfect gases.

The quantity flowing per unit of time is given by the continuity equation,

$$M = A_2w_2/V_2 \tag{4}$$

and, since the expansion is a reversible adiabatic (see page 73),

$$\frac{V_2}{V_1} = \left(\frac{T_1}{T_2}\right)^{\frac{1}{k-1}} = \left(\frac{P_1}{P_2}\right)^{\frac{1}{k}} \tag{5}$$

Then,

$$M = \frac{A_2}{V_1}\sqrt{2gc_PT_1\left[\left(\frac{T_2}{T_1}\right)^{\frac{2}{k-1}} - \left(\frac{T_2}{T_1}\right)^{\frac{k+1}{k-1}}\right]} \tag{6}$$

or

$$M = \frac{A_2}{V_1}\sqrt{2gc_PT_1\left[\left(\frac{P_2}{P_1}\right)^{\frac{2}{k}} - \left(\frac{P_2}{P_1}\right)^{\frac{k+1}{k}}\right]} \tag{7}$$

The differential of M with respect to T_2, T_1 or P_2 P_1 when equated to zero indicates that the flow rate M is a maximum when

$$\frac{T_2}{T_1} = \frac{2}{k+1} \quad \text{and} \quad \frac{P_2}{P_1} = \left(\frac{2}{k+1}\right)^{\frac{k}{k-1}} \tag{8}$$

For temperatures near those of the atmosphere, $k = 1.4$ and

$$T_2/T_1 = 0.833 \quad \text{and} \quad P_2/P_1 = 0.528^*$$

Thus, the maximum rate of flow of a gas through an orifice for any given initial conditions is attained when $P_2 = 0.528P_1$. This is termed the *critical pressure.* A lower back pressure will not increase the rate of flow through the orifice.

Example.—Determine the theoretical maximum rate at which air will flow through an orifice 1 in.^{2} in area. The orifice discharges air from a tank into the atmosphere. The pressure in the tank is 150 lb/in.^{2} abs and the temperature of the air in the tank is 100 F.

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* The critical pressure is slightly higher for actual gases (see the section on Vapors). Also deviations in V, H, and S must be considered in solving the Energy Equation for the *kinetic energy* and velocity, and in solving the continuity equation for the mass flow if the medium deviates appreciably from the perfect-gas condition.

The critical pressure will be used since the back pressure is less than the critical pressure. Thus $P_2 = 0.528 \times 150 = 79.2$ lb/in.²

$$V_1 = \frac{RT_1}{P_1} = \frac{1545 \times 560}{150 \times 144} = 40.1 \text{ ft}^3\text{/mole of air}$$

Since the kinetic energy is in foot-pounds per pound, the dimensions of c_p must be the same. From Table II, Appendix, at 560°R,

$$c_p = 6.936 \text{ Btu/mole} = \frac{6.936 \times 778}{28.97} = 186.3 \text{ ft-lb/lb}$$

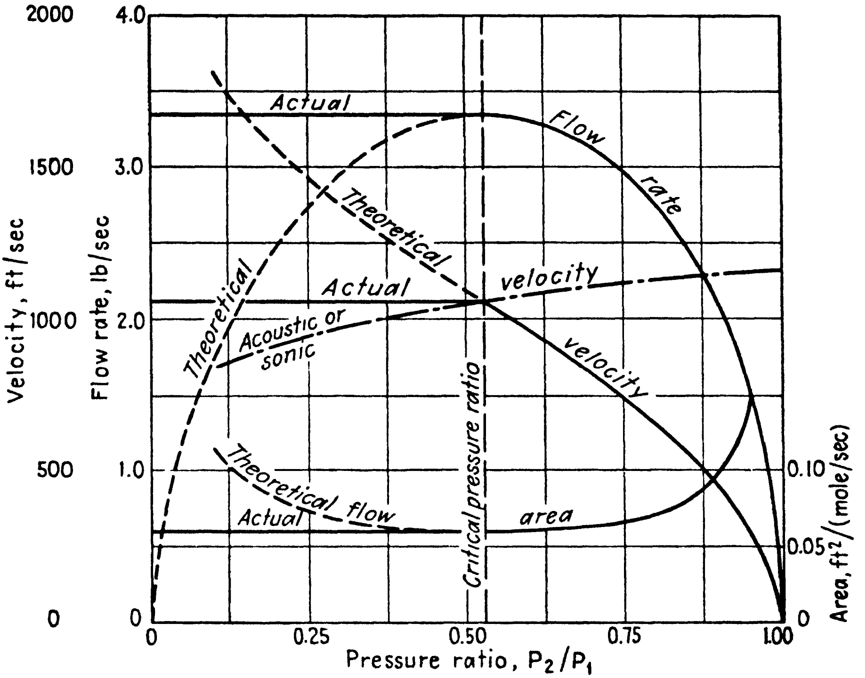


FIG. 125.—Theoretical and actual flow through a well-rounded orifice. Medium is air. Negligible velocity of approach. Initial conditions: $P_1 = 150$ lb/in.² abs. and $T_1 = 560°$ R. Orifice area = 1 in.²

Then substituting in Eq. (7)

$$M = [(1/144)/40.1] \sqrt{2 \times 32.2 \times 186.3 \times 560\,[(0.528)^{1.429} - (0.528)^{1.714}]}$$

$$= 0.449 \sqrt{(0.401 - 0.335)} = 0.1154 \text{ mole/sec}$$

$$0.1154 \text{ mole/sec} \times 28.97 \text{ lb/mole} = 3.34 \text{ lb/sec}$$

In a similar manner the flow rates for other pressure ratios may be determined (Fig. 125). Obviously, the flow rate does not decrease to zero as the downstream pressure is decreased to zero pressure. This can be verified experimentally and results in maximum flow at and below critical pressure ratios.

The maximum velocity of flow attainable in an orifice is the *acoustic* or *sonic* velocity for the medium. The relation for this velocity may be obtained by combining the equation for w_2 with the critical pressure-ratio relations and the Equation of State. This results in

$$w_2 = w_c = \sqrt{gkP_2V_2} = \sqrt{gkRT_2} \tag{9}$$

for a perfect gas, assuming constant specific heat.

The critical pressure ratio for flow through orifices or nozzles is the result of an inherent characteristic of gases and vapors that is indicated by the theoretical flow area (Fig. 125). As the pressure on the downstream side of the orifice is lowered below the upstream pressure (down to the critical pressure) the velocity of flow increases faster than the specific volume and less orifice area is required to flow a given amount of fluid. However, as the back pressure is lowered below the critical pressure, the specific volume increases faster than the velocity and more area is required to flow the given amount of medium. Hence, the increase in specific volume of the fluid restricts the flow through orifices for pressure drops below the critical pressure. Also, the effect of the pressure on the downstream side, when below the critical pressure, cannot be transmitted upstream and increase the specific volume since the fluid is flowing from the orifice with the acoustic velocity. This phenomenon prevents the flow from decreasing to zero as the back pressure is lowered below the critical pressure, although this is indicated by the mathematical relationship (Eq. 7).

The *sonic* velocity of the medium is higher than the flow velocity above critical pressure ratios (Fig. 125) and lower below critical pressure ratios. The high flow velocities (supersonic) are attained in the diverging section of nozzles.

Actual velocities and rates of flow are determined by multiplying the theoretical values by the coefficients of jet contraction and velocity (see page 248).

If the pipe line ahead of the orifice is not sufficiently large, the initial velocity w_1 must be considered. The term w_1 may be eliminated by means of the continuity equation. Thus

$$w_1 = w_2A_2V_1/A_1V_2 \tag{10}$$

Also, for perfect gases, $$V_1/V_2 = (P_2/P_1)^{1/k} \tag{11}$$

Substituting Eqs. (10) and (11) in Eq. (2) results in

$$w_2 = \sqrt{\frac{2gc_p\,(T_1 - T_2)}{1 - (A_2/A_1)^2(P_2/P_1)^{\frac{2}{k}}}} \tag{12}$$

and

$$M = A_2/V_1\sqrt{\frac{2gc_pT_1\left[(P_2/P_1)^{\frac{2}{k}} - (P_2/P_1)^{\frac{k+1}{k}}\right]}{1 - (A_2/A_1)^2(P_2/P_1)^{\frac{2}{k}}}} \tag{13}$$

Differentiating M with respect to P_2/P_1 and equating to zero result in the following expression for the maximum rate of flow and pressure ratio across the orifice:

$$\frac{k-2}{2}\left(\frac{A_2}{A_1}\right)^2\left(\frac{P_2}{P_1}\right)^{\frac{2}{k}} + \left(\frac{P_2}{P_1}\right)^{\frac{1-k}{k}} = \frac{k+1}{2} \tag{14}$$

Assuming A_1/A_2 is infinite, Eq. 14 becomes identical with Eq. 8. Also, the critical pressure ratio decreases slowly as the value of A_1/A_2 is decreased from infinity to 5, being below 0.5 at a value of 2 and decreasing rapidly toward 0 as A_1/A_2 approaches zero. It should be noted that below a value of A_1/A_2 of 1, the orifice is an expanding tube.

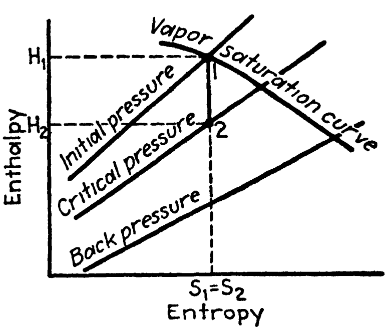


Fig. 126.—Enthalpy-entropy diagram for H drop through an orifice

Vapors.—The Energy Equation for the flow of vapors through orifices is the same as that for gases. Thus,

$$(w_2^2 - w_1^2)\ 2g = H_1 - H_2 \tag{1}$$

and, if w_1 is negligible,

$$w_2 = \sqrt{2g(H_1 - H_2)} \tag{2}$$

The maximum rate of flow of vapors through an orifice occurs at pressure ratios ranging from about 0.55 to about 0.58 depending on the condition of the vapor and assuming a negligible velocity of approach. The value 0.58 applies to wet or saturated vapor while 0.55 applies to highly superheated vapors. These values decrease with an increase in superheat toward the value of 0.53, the critical pressure ratio for perfect gases.

The decrease in H for this process, for a given decrease in pressure, may be determined from the Mollier diagram for the medium (Fig. 126). The flow is assumed to be a reversible adiabatic process because of the short length of the orifice.

Example.—Determine the maximum rate at which water vapor will be discharged into the atmosphere from a pressure of 100 lb/in.² abs. The area of the orifice is 1 in.², and the steam is initially saturated.

From the Mollier diagram, Chart A, Appendix,

At 100 lb/in.^{2} and saturated, $H_1 = 1187.2$ Btu/lb
At 58 lb/in.^{2} and S_1. $H_2 = 1144.0$ Btu/lb
Then,

$$w_2 = \sqrt{2 \times 32.2(1187.2 - 1144.0)\,778}$$
$$= 1{,}471 \text{ ft/sec}$$

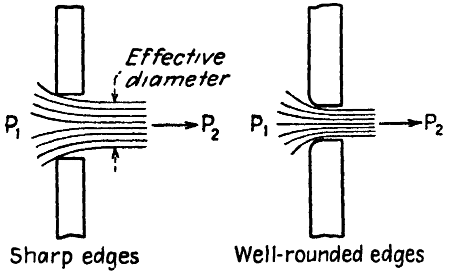
At 58 lb/in.^{2} and final conditions ($S_2 = S_1$) the value of x is 0.964.

Also, $V_2 = [V_g - (1 - x)V_{fg}]_2 = 7.407 - 0.036 \times 7.390 = 7.141$ ft^3/lb

Then,

$$M = \frac{A_2 w_2}{V_2} = \frac{1 \times 1471}{144 \times 7.141} = 1.43 \text{ lb/sec}$$

Orifice Coefficients.—The foregoing treatment of flow through orifices is based upon the assumptions that the fluid fills the orifice and that no friction effects occur. Orifices with sharp edges (Fig. 127) cause the jet of fluid to contract. This is the result of the various flow lines of the fluid approaching the orifice. The jet contraction reduces the effective area of the jet to about 0.60 of the orifice area when the area of the orifice is small compared to the area of cross section of the reservoir or pipe to which the orifice is attached.



Sharp edges Well-rounded edges

FIG. 127.—Flow through sharp-edged and well-rounded orifices. (Back pressure above the critical pressure.)

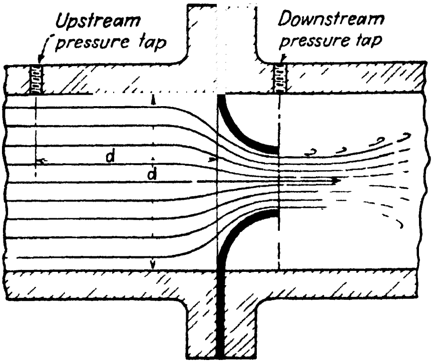


FIG. 128.—Location of pressure taps for well-rounded orifice or flow nozzle in pipe line.

Rounding the orifice on the side of the approaching fluid (Fig. 127) causes the jet to fill the orifice. In such cases the coefficient of jet contraction based on the orifice area is practically unity. Thus, this coefficient may vary from 0.60 to practically unity depending on the upstream side of the orifice and the relative size of the orifice and the pipe in which it is located.

The velocity coefficient is the ratio of the actual to the theoretical velocity. Since orifices are relatively small in length, the friction effect is usually very small and results in a decrease of 1 to 2 per cent in velocity. Thus, this coefficient is usually about 0.98 to 0.99.

The flow coefficient is the product of velocity and jet contraction coefficients. Thus

$$w_{\text{actual}} = c_{\text{vel}} \sqrt{2g(H_1 - H_2) + w_1^2} \tag{1}$$

$$A_{\text{effective}} = c_{\text{jet cont}} A_{\text{actual}} \tag{2}$$

$$M_{\text{actual}} = (cAw/V) \tag{3}$$

where c is the coefficient of flow, and V is the specific volume of the fluid.

The flow coefficients for sharp-edge thin-plate orifices in pipe lines depend on velocity of approach, pipe size, orifice-pipe diameter ratios, and the Reynolds number for the flow.*

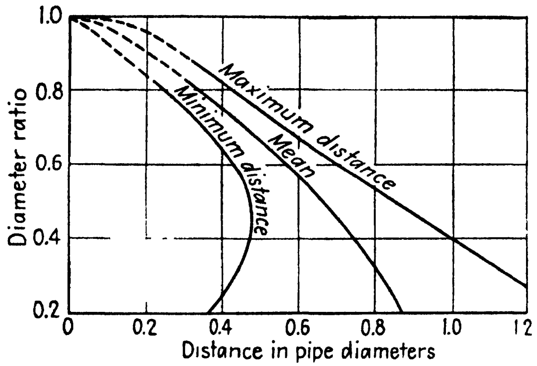


FIG. 129.—Location of minimum static pressure for sharp-edge thin-plate orifices. For 2-in. or larger pipe. (Fluid Meters, Part I, 4th ed., A.S.M.E., 1937.)

Orifices in Pipe Lines.—Flow through orifices into the atmosphere or into a large chamber indicates that the pressure of the flowing medium drops to atmospheric or chamber pressure, respectively, and these pressures are used for flow evaluations. A well-rounded orifice† (Fig. 128) streamlines the flow so that no contraction of the jet occurs beyond the orifice. Thus, in pipe lines, it is customary to determine the downstream pressure at the plane of the discharge section of the well-rounded orifice, while the upstream pressure is determined at a position about one pipe diameter ahead of the plane of the upstream section of the orifice. The location of the downstream pressure tap is based on the assumption that at minimum jet section the maximum velocity and minimum pressure occur.

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* See "Fluid Meters," Part I, 4th ed., A.S.M.E., 1937, for very complete information on flow coefficients.

† It has been suggested that this be termed a *nozzle* or *flow nozzle*. *Ibid.*

The location of the minimum jet section or *vena contracta* for flow through a sharp-edge or thin-plate orifice depends on the ratio of orifice to pipe diameter (Fig. 129).

FLOW THROUGH NOZZLES, DIFFUSERS, AND RAM CHAMBERS

General.—The flow of a fluid through an orifice will be very nearly laminar and free from turbulence, if the orifice is well rounded and the back pressure is equal to or greater than the critical pressure. With back pressures lower than the critical pressure, the jet of vapor or gaseous fluid tends to explode as it leaves the orifice at the critical pressure and enters the region of lower pressure. This explosive tendency of a vapor or gaseous jet can be eliminated by adding an expanding section to the orifice as indicated by the Theoretical Flow Area in Fig. 125. This permits the fluid to expand gradually to the back pressure and effectively directs the fluid stream as its velocity increases. The combination of the well-rounded orifice and the expanding tube is termed a *nozzle* or a converging-diverging nozzle (Fig. 132).

The friction in the orifice section of a nozzle is very small and is usually neglected. However, the larger rubbing surface and higher velocities make the friction in the expanding section of the nozzle an important factor. This friction effect results in an increase in entropy and a reduction of the enthalpy change of the medium for a given pressure drop through the nozzle.

Flow through nozzles is analyzed by dealing first with the flow through the orifice section, and then by dealing with either the flow through the expanding section or the flow through the entire nozzle.

Through the orifice,

$$(w_t^2 - w_1^2)/2g = H_1 - H_t \tag{1}$$

and

$$M = A_t w_t / V_t \tag{2}$$

where the subscript 1 indicates the section ahead of the nozzle, and t indicates the *smallest section* or *throat* of the nozzle. The area of the throat determines the value of M, the *rate of flow* through the nozzle.

Through the expanding section,

$$(w_e^2 - w_t^2)/2g = H_t - H_e \tag{3}$$

and

$$M = A_e w_e / V_e \tag{4}$$

where the subscript e indicates the *exit section* of the nozzle.

Through the entire nozzle

$$(w_e^2 - w_1^2)/2g = H_1 - H_e \tag{5}$$

Eq. (4) being applicable again to the exit section.

It is customary to analyze the nozzle as a whole when determining the exit velocity w_e, and to relate the actual enthalpy drop to the ideal drop by a factor y which indicates the part of the reversible adiabatic enthalpy drop which is first transformed to kinetic energy and then reconverted into enthalpy by the friction process. Thus,

$$H_1 - H_e = (H_1 - H_2)_s(1 - y) \tag{6}$$

from which

$$(w_e^2 - w_1^2)/2g = (H_1 - H_2)_s(1 - y) \tag{7}$$

or, if w_1 is negligible,

$$w_e = \sqrt{2g(H_1 - H_2)_s(1 - y)} \tag{8}$$

in which $(H_1 - H_2)_s$ is the change in enthalpy resulting from the reversible adiabatic drop in pressure through the nozzle.

Example.—Air is discharged through a nozzle having a throat area of 1 in.^{2} The initial pressure is 150 lb/in.^{2} abs and the back pressure is 15 lb/in.^{2} abs. $T_1 = 100$ F; $y = 0.15$ of the ideal H drop for the nozzle. Determine the area of the mouth of the nozzle.

From the example on page 245 for which the same data were used, it was found that the quantity discharged through the orifice was 0.1154 mole/sec. This is also the quantity that will be discharged through the nozzle.

The temperature of the medium at the exit of the nozzle, with no friction, would be

$$T_e = T_1\left(\frac{P_e}{P_1}\right)^{\frac{k-1}{k}} = 560\left(\frac{15}{150}\right)^{\frac{0.4}{1.4}} = 290°\text{R}$$

assuming constant specific heat* for this temperature range,

$$\begin{aligned} w_e &= \sqrt{2gc_P(T_1 - T_e)_s(1 - y)} \\ &= \sqrt{2 \times 32.2 \times 186.4(560 - 290)(1 - 0.15)} = 1660 \text{ ft/sec} \end{aligned}$$

The area of the exit section of the nozzle is determined from the conditions existing at that section. Although the pressure has dropped to 15 lb/in.^{2}, the temperature is actually higher than 290°R because of the effect of friction (Fig. 130). Since 0.15 of the ideal H drop did not appear as final kinetic energy,

$$H_e = (H_1 - H_2)_s y + H_2$$

or with constant specific heat,

$$\begin{aligned} T_e &= (T_1 - T_2)_s y + T_2 \\ &= (560 - 290)0.15 + 290 = 331°\text{R} \end{aligned}$$

The specific volume of the air at the conditions actually existing at the exit of the nozzle will be

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* Variable specific heat must be considered for temperatures appreciably higher than atmospheric. In such cases values of H can be obtained directly from Table XIX in the Appendix. Also, the entropy tables may be used to determine T_2 if it is not below the lowest temperature in the table.

$$V_e = \frac{RT_e}{P_e} = \frac{1{,}545 \times 331}{15 \times 144} = 236.7 \text{ ft}^3/\text{mole}$$

Then,
$$A_e = \frac{MV_e}{w_e} = \frac{0.1154 \times 236.7}{1{,}660} = 0.0165 \text{ ft}^2 = 2.38 \text{ in.}^2$$

The flow of vapor through a nozzle is analyzed in the same manner with the use of the proper vapor tables or diagrams.

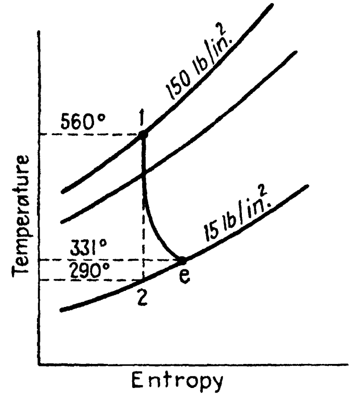

FIG. 130.—*T-S* diagram for gas flow through a nozzle.

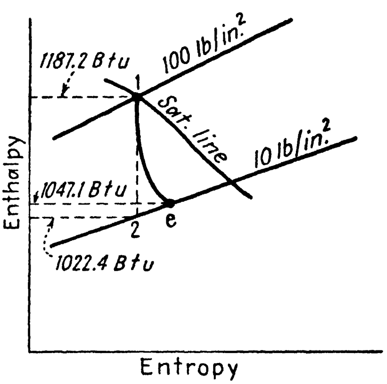

FIG. 131.—*H-S* diagram for vapor flow through a nozzle.

Example.—Determine the area of the exit of a steam nozzle having a throat area of 1 in.² The back pressure is 10 lb/in.² abs, and y is 0.15 of the ideal H drop. The steam is initially saturated at 100 lb/in.² abs pr.

From the example on page 248 for which the same data were given, it will be noted that the quantity discharged will be 1.43 lb/sec.

From the Mollier diagram for water vapor, Chart A, Appendix, and Fig. 131, H_2 at s_1 is found to be 1022.4 Btu. Then,

$$\begin{aligned} w_e &= \sqrt{2 \times 32.2 \times 778(1187.2 - 1022.4)(1 - 0.15)} \\ &= 2{,}648 \text{ ft/sec} \end{aligned}$$

Also, $H_e = (H_1 - H_2)_s y + H_2 = (1187.2 - 1022.4)0.15 + 1022.4 = 1047.1$ Btu

A value of $H = 1047.1$ Btu at a pressure of 10 lb/in.² abs indicates a value of $(1 - x)$ of 0.0978. Then,

$$V_e = [V_g - (1 - x)V_{fg}]_{10\ \text{lb/in}^2} = 38.42 - 0.0978 \times 38.40 = 34.66 \text{ ft}^3/\text{lb}$$

and
$$A_e = MV_e/w_e = 1.43 \times 34.66/2648 = 0.0187 \text{ ft}^2 = 2.70 \text{ in.}^2$$

In a similar manner the pressures at various sections of the diverging part of the nozzle were determined by assuming values of y of 0.10, 0.06, and 0.03 for pressures of 20, 30, and 40 lb/in.², respectively. The areas computed for these values indicated the sections at which the various pressures occur (Fig. 132). The pressure at the throat of the nozzle is the critical pressure for discharge pressures ranging from the designed pressure up to about 0.8 the initial pressure. For discharge pressures in the foregoing range, the flow undergoes a *pressure shock* at some section in the diverging part of the nozzle. At this point the pressure changes very abruptly while the velocity changes from supersonic to subsonic velocities. Beyond this point the diverging tube acts as a diffuser, and the velocity decreases gradually as the pressure rises to the end of the nozzle.

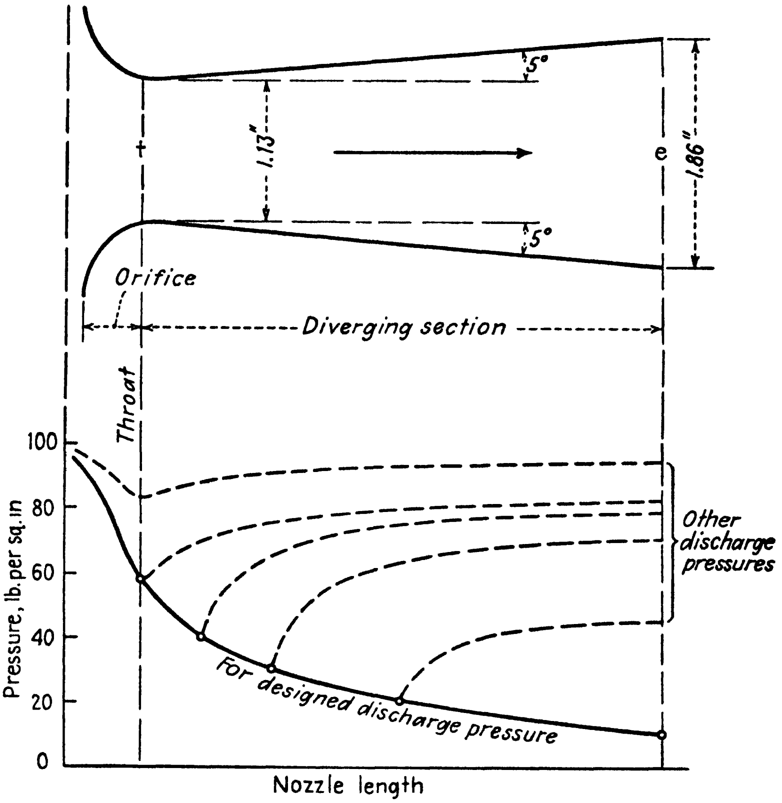

FIG. 132.—Pressure conditions in a nozzle with discharge pressures for and above that for which it was designed. Initial conditions saturated steam at 100 lb/in.^{2}

The pressure attainable in a sudden transformation from supersonic to subsonic velocities may be determined by applying the Energy, Continuity, and Momentum Equations to the process. Assuming an adiabatic process,

$$H_1 + KE_1 = H_2 + KE_2 \tag{9}$$

in which subscripts 1 and 2 indicate conditions immediately before and after shock.

A sudden or instantaneous transformation indicates a very thin section in which the shock occurs. Hence the flow areas are assumed to be the same before and after shock, and

$$M = Aw_1/V_1 = Aw_2/V_2 \tag{10}$$

With known conditions at point 1, an assumption of H_2 permits the evaluation of KE_2 (and w_2)* from Eq. (9), and the evaluation of V_2 from Eq. (10). Thus, for every assumed H_2 there is a corresponding V_2, and consequently P_2, that satisfy the Energy and Continuity Equations. The locus of such a series of points is termed a *Fanno line*.†

The combination of P_2 and w_2 that satisfies the Momentum Equation

$$(P_2 - P_1)A = (M/g)(w_1 - w_2) \tag{11}$$

indicates the pressure and velocity after the pressure shock.

The entropy of the medium after adiabatic shock is more than before the process, indicating an irreversible effect. Hence, an abrupt decrease in pressure is impossible, since reversing the foregoing analysis would indicate a decrease in entropy for an adiabatic process.

At discharge pressures above about 0.8 of the initial pressure up to almost the initial pressure, the pressure at the throat ranges from the critical pressure upward but is always appreciably below the discharge pressure. Under this condition of operation the nozzle acts as a venturi which is often used to measure flow since the throat causes an appreciable increase in velocity of flow with a corresponding pressure drop which may be used to compute flow, while the diverging section reconverts most of the velocity head at the throat into pressure head at the end section. Thus, only a small pressure loss need be incurred with venturi meters.‡

Nozzles for Turbines.—Nozzles for turbines are usually set at an angle to the plane of rotation of the turbine blades. Although the nozzle is designed with an exit section at *BB′* (Fig. 133), the edge *AB* may be extended to *C* and the edge *A′B′* cut back to *C′* so that the mouth section may be represented by *CC′*. In this case the vapor along the side *A′C′* is not fully expanded when it leaves the nozzle. Hence, it is considered desirable to extend the side AB to D, adding a *cylindrical* or rectangular extension BDB' to the nozzle proper, merging the conical section gradually into the extension. The addition of extension $BEE'B'$ tends to straighten the diverging jet and direct it as a cylindrical or rectangular stream toward the turbine blades.

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* The use of a value of w_2 corresponding to KE_2 in Eq. (10) indicates an assumption of no eddy velocities, *i.e.*, all the fluid has the same velocity and it is in a direction perpendicular to the flow area.

† STODOLA, A., (LOEWENSTEIN), "Steam and Gas Turbines," Vol. I, p. 61, McGraw-Hill Book Company, Inc., New York, 1927.

‡ The venturi meter usually has a converging conical section instead of an orifice ahead of the throat (see reference, p. 249).

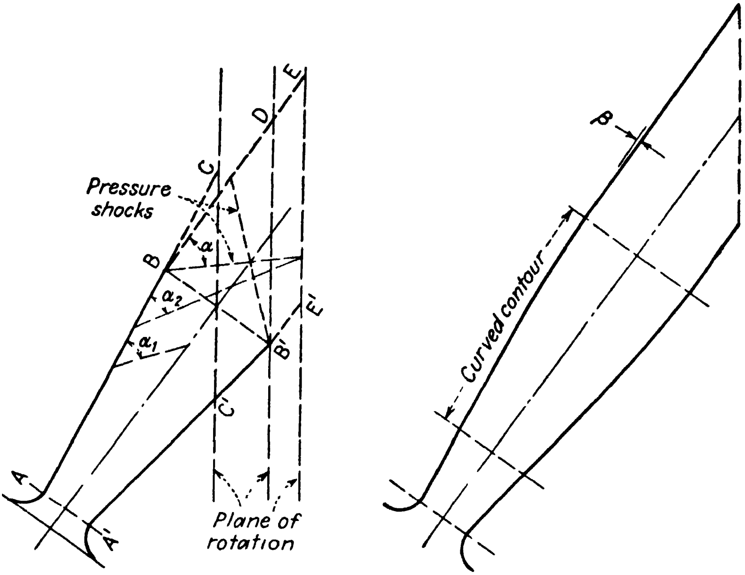

Fig. 133.—Nozzle and extension for turbine use. (With straight and curved contours.)

The abrupt change from the diverging section of the nozzle to the cylindrical section (Fig. 133) sets up a pressure shock, when the fluid velocity is supersonic, at the Mach lines indicated by the angle α, when α is defined as follows:

$$\sin \alpha = w_c/w = 1/\mathrm{M} \tag{1}$$

in which w_c and w are acoustic (sonic) and stream velocity, respectively, and M is the Mach number.

In the expanding section of the nozzle the stream velocity is increasing and the acoustic velocity is decreasing. Thus, α is decreasing along the line of flow and the adjacent Mach lines (indicated by α_1 and α_2) do not intersect and shock fronts are not formed. However, all those Mach lines between the two indicated by α_2 and α do intersect and set up the shock front at the Mach line indicated by α. The introduction of a curved contour connecting the diverging cone with the cylindrical end section is used to reduce pressure shock to a desirable minimum by designing the curved contour* (Fig. 133) to eliminate intersection of Mach lines and shock except where it joins the cylindrical section where the surfaces intersect at a small angle.

Jet Reaction or Propulsive Effect.—A jet of fluid flowing from a nozzle produces a reaction on the nozzle or the chamber to which the nozzle is attached. This reaction or thrust depends on the entering and leaving velocities and their directions. In the case of the *rocket* (Fig. 134) which carries all of its propelling medium, the velocity of the medium is zero relative to the rocket before reaction in the burner, whether the rocket is in motion or not. The medium is accelerated from zero velocity to the velocity, w_2, with which the medium leaves the nozzle of the rocket. Thus, for a flow rate of M lb per sec, the force required to accelerate the medium is

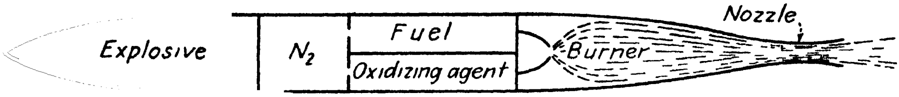

FIG. 134.—Diagrammatic sketch of explosive rocket

$$F = (M/g)(w_2 - 0) \tag{1}$$

which is the jet-propulsive or thrust effect of a fluid issuing from any device.

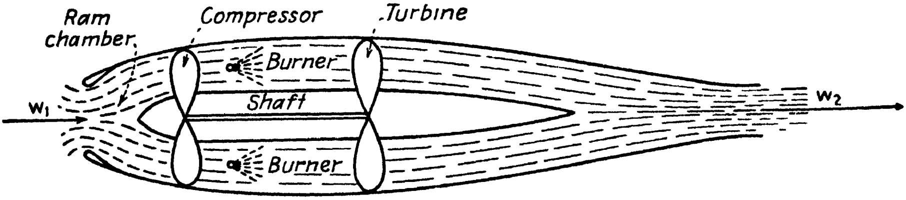

FIG. 135—Diagrammatic sketch of a jet-propulsion unit

A jet-propelled plane has air entering the propulsion unit (Fig. 135) during flight at a velocity, relative to the plane, equal to the air speed of the plane. The air is compressed first in the ram chamber and then in the compressor; fuel is added and burned; the hot gases produce turbine work to drive the compressor and then leave the unit with a high velocity. The air is accelerated from w_1 to w_2, while the fuel is accelerated from 0 to w_2. Assuming that the entering and leaving velocities are in the same direction and along the line of flight, the net propulsive force is

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* SHAPIRO, A. H., "Nozzles for Supersonic Flow Without Shock Fronts," *Trans., A.S.M.E.*, **66**, A, 93 (1944).

$$F = [(M + m)w_2 - Mw_1]/g \tag{2}$$

where M and m are the flow rates of the air and fuel, respectively, and w_1 and w_2 are the entering and leaving velocities, respectively.

For cases of converging nozzles and atmospheric pressures below the critical back-pressure value, an additional force occurs because of the incomplete expansion of the jet. This force is equivalent to the product of the critical minus the atmospheric pressure and the nozzle exit area.

$$\text{Force} = (P_c - P_{\text{atm}})A_e \tag{3}$$

In like manner, the drag of ram chambers or cooling air ducts on planes may be evaluated from the entering and leaving velocities and the air flow rate. The heat added to the cooling air stream, after being rammed to a relatively low velocity, can be used to offset some of the drag by the expansion of the air to atmospheric pressure in properly designed passageways before leaving the plane. In some cases a zero drag or even a small net thrust may be obtained.

Supersaturated Vapor.[*]—The flow of a vapor through an orifice or a nozzle occurs so rapidly that an unstable condition exists as regards the pressure-temperature relationship in the saturated region. Also, condensation does not occur when the expansion process crosses the saturation curve, but the vapor acts like a gas at least until the pressure is about one-half that at which the process crosses the saturation curve. This *supersaturated* condition, with a temperature lower than that corresponding to the pressure, results in a lower specific volume and larger rate of discharge than would be expected with the assumption of equilibrium conditions.

This increase in rate of discharge which may be of the order of 2 to 3 per cent results in a coefficient of discharge of unity or above when based upon the ideal equilibrium flow computations. The usual method for accounting for supersaturation of H_2O vapor in flow through an orifice is to assume that the expansion follows a path indicated by

$$PV^{1.3} = \text{const}$$

and to solve for the flow in the same manner as for gases.

Ram Chambers.—The flow through ram chambers is analyzed in a manner similar to that for flow through nozzles except that the flow is reversed and the pressure of the fluid increases as the velocity of flow is decreased. If the initial fluid velocity is sonic or subsonic, the ram chamber is in general the reverse of a well-rounded orifice, *i.e.*, increasing in section area from the entrance to the exit sections. The entrance is well rounded, the length is appreciably longer than an orifice of the same diameter, and the expanding section is gradually rounded into the maximum section area.

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[*] STODOLA, *op. cit.*, p. 117.

For supersonic initial fluid velocities, the entrance of the ram chamber is sharp-edged and the reduction to sonic velocity is accomplished in a chamber which decreases in section, *i.e.*, the reverse of the expanding section of a nozzle. The reduction in fluid velocity from sonic to subsonic is accomplished in the next section of the ram chamber which increases in section area as indicated in the foregoing. This construction is indicated by the relation between the theoretical velocity and flow areas in Fig. 125, which indicates a minimum flow area for sonic velocity.

The effect of friction in ram chambers is to reduce the pressure rise and increase the entropy (Fig. 138).

The *ejector* is a combination of a nozzle and a ram chamber in which the actuating fluid inducts and compresses another fluid. Thermodynamic analysis* of the fluid flow in this device necessitates the use of some of the relations in this chapter and in the Appendix.

FLOW OVER TURBINE AND COMPRESSOR BLADES†

The flow of a fluid over moving blades results in the transformation of kinetic energy of the fluid into mechanical work or vice versa. The blades must be curved or shaped so that the fluid flowing over the blades has its direction changed and thereby exerts a *force* on the blades. The blades must also move so that the force on the blades acts through a *distance* in the case of the turbine, or the blades must be moved against the force in the case of the compressor. Thus no mechanical work is done in flowing a fluid over stationary blades that merely serve to give the fluid the desired direction to approach the moving blades, and in some cases provide passageways in which the medium may change in pressure while undergoing a change in velocity.

All flow requires a pressure drop to maintain or increase velocity of flow. The length of axial turbine blades along the line of flow is comparatively short so that under certain conditions it may be assumed that no pressure drop occurs across a given set of blades. In other cases, the passageways are so designed that pressure drop occurs during flow of the fluid over either or both the stationary and moving blades.

Compressors are designed to raise the pressure of the medium as it flows over both the moving and stationary blades.

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* Elrod, Jr., H. G., "The Theory of Ejectors," *Trans.*, *A.S.M.E.*, **65**, A-170 (1945).

† Nominal friction effects are assumed in the various illustrative examples. See Church, E. F., "Steam Turbines," 2d ed., McGraw-Hill Book Company, Inc., New York, 1935, for friction factors, etc., for cases in which shock effects occur because of incorrect blade angle or speed.

Stationary Blades; No Pressure Change.—Stationary blades form curved channels through which the fluid flows (Fig. 136) and, if no pressure change occurs, these blades are termed *guide vanes.* The fluid enters the blades with an initial kinetic energy and is assumed to leave with the same kinetic energy if friction is neglected. This implies constant cross-sectional area of the channels perpendicular to the line of flow between the blades, or the same cross-sectional area at entrance and exit positions. However, the change of direction of the flowing fluid causes it to exert a pressure on the blade which results in appreciable fluid friction. This decreases the kinetic energy and increases the enthalpy of the fluid at constant pressure. The Energy Equation is

$$KE_1 + H_1 = KE_2 + H_2 \qquad (1)$$

or

$$(w_1^2 - w_2^2)/2g = H_2 - H_1 \qquad (2)$$

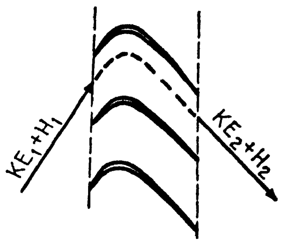

FIG. 136.—Flow over stationary blades.

The effect of friction is to reduce the velocity or kinetic energy. Thus, if y represents the fraction of the initial kinetic energy that is dissipated by friction

$$w_2^2/2g = (1 - y)w_1^2/2g \qquad (3)$$

or

$$H_2 - H_1 = yw_1^2/2g \qquad (4)$$

from which the effect of the friction process may be evaluated in terms of the increase in enthalpy of the fluid flowing over the stationary blades. Values of y are about of the order of 0.05 to 0.10 depending on the fluid conditions, the blade shape, and the amount of rubbing surface per unit quantity of fluid.

Example.— Determine the final condition of H_2O after flowing over a row of stationary blades. The initial condition of the H_2O is 14.7 lb/in.² abs pr and a quality of 0.9 0 The initial velocity is 1,000 ft/sec; $y = 0.07$.

$$H_2 - H_1 = y\frac{w_1^2}{2g} = 1 \text{ lb} \times 0.07 \times \frac{\overline{1{,}000}^2 \text{ ft}^2/\text{sec}^2}{2 \times 32.2 \text{ ft/sec}^2}$$

$$= 1{,}087 \text{ ft-lb/lb} = 1.4 \text{ Btu/lb}$$

At 14.7 lb/in.² pr and $x = 0.90$, $H = 1053.4$ Btu/lb.

$$H_2 = 1053.4 + 1.4 = 1054.8 \text{ Btu/lb}$$

At 14.7 lb/in.² pr and $H = 1054.8$ Btu/lb, $x = 0.902$.

Also, $$w_2 = \sqrt{2g(1 - y)\frac{w_1^2}{2g}} = \sqrt{0.93 \times \overline{1{,}000}^2 \text{ ft}^2/\text{sec}^2} = 965 \text{ ft/sec}$$

Example.—Determine the temperature rise of air after flowing over a row of stationary blades. The initial velocity is 1,000 ft/sec and y is 0.07. T_1 is 100 F.

The foregoing example indicates that ΔH will be 1.4 Btu/lb of fluid. The specific heat at constant pressure for air is approximately 7 Btu/mole or 0.24 Btu/lb. Thus

$$\Delta T = 1.4/0.24 = 5.8 \text{ F}$$

These two examples indicate that the flow area should increase from the entering to the leaving edge of the blades since the velocity decreases and the specific volume of the fluid increases as the fluid flows through the passageway between the blades.

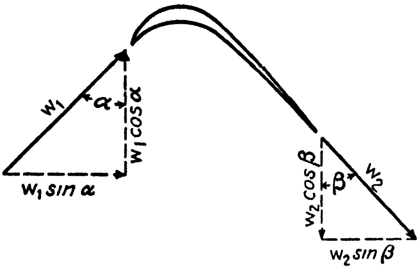

Fig. 137.—Effect of blade on velocity and velocity components

The force exerted on the blade depends on the change in momentum that the fluid undergoes in flowing over the blade. The fluid should approach the blade in a direction tangential to its entering edge. The shape of the blade changes the direction of the velocity of the fluid and consequently changes the velocity components.

The entering fluid has a velocity component (Fig. 137) of $w_1 \cos \alpha$ in the vertical direction. The leaving fluid has a velocity component $w_2 \cos \beta$ in the opposite direction.

These vector quantities are opposite in sign and consequently are added to determine the change in momentum. Thus, for 1 lb of fluid flowing over the blades per second, the force on the blades in the vertical direction will be

$$F = (w_1 \cos \alpha + w_2 \cos \beta)/32.2 \tag{5}$$

Example.—Assume that the entering and leaving angles of a stationary blade, measured from the vertical axis (Fig 137) are 45 and 30 deg, respectively. Determine the force exerted in a vertical direction on the blade per pound of medium per second for the same conditions as in the preceding example

From the preceding example, w_2 = 1,000 ft/sec, and w_2 = 965 ft/sec.

Then, $F = (w_1 \cos \alpha + w_2 \cos \beta)/32.2$

$= (1{,}000 \times 0.707 + 965 \times 0.866)/32.2 = 47.9$ lb/(lb/sec)

The force to the right in a horizontal direction (Fig. 137) will be

$$F = (w_1 \sin \alpha - w_2 \sin \beta)/32.2 \tag{6}$$

Since the blade is stationary, none of the forces on the blade results in work.

Stationary Blades; Pressure Change.—The passageways between stationary blades in which pressure change occurs are used to produce either a *nozzle* or a *diffuser* effect. A drop in pressure as a fluid flows over stationary blades tends to increase the velocity of the fluid, while the friction effect of the fluid rubbing against the blades tends to reduce the velocity increase of the fluid.

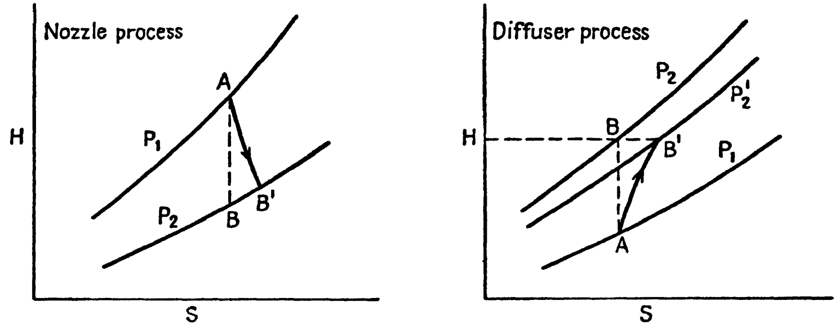

FIG. 138.—*H-S* diagrams for pressure change with flow over stationary blades

An increase in pressure as the fluid flows over the stationary blades results from the decrease in velocity of the fluid flowing. Any friction effect reduces the pressure increase of the fluid. The Energy Equation for both the nozzle and diffuser processes is

$$KE_1 + H_1 = KE_2 + H_2 \tag{1}$$

The path followed on the *H-S* diagram for the nozzle process, without the friction effect, would be *AB* (Fig. 138). The path *AB′* is the usual case in which the effect of friction is appreciably smaller than the effect of pressure drop on the change of kinetic energy of the fluid.

In the case of relatively low initial velocities and high pressure drops the analysis is the same as set forth for nozzles. For high initial velocities and small pressure drops the friction effect is based on the initial kinetic energy for both the nozzle and diffuser processes. If y is the portion of the initial kinetic energy that undergoes friction transformation,

$$H_1 - H_2 = H_A - H_{B'} = (H_A - H_B) - y(w_1^2/2g) \tag{2}$$

Substituting in Eq. (1) results in

$$[w_2^2 - (1 - y)w_1^2]/2g = H_A - H_B \tag{3}$$

when $H_A - H_B$ is the adiabatic frictionless H change for the given pressure change.

The areas of the entering and leaving sections of the channels between the *stationary* blades can be determined from the velocities and fluid conditions at the entrance and exit sections of the blades. The areas should be determined perpendicular to the line of flow.

Example.—H_2O at 14.7 lb/in.^{2} abs pr and a quality of 0.90 enters a row of stationary blades with a velocity of 1,000 ft/sec. The pressure drops to 12 lb/in.^{2} abs in flowing over the blades. Ten per cent of the initial kinetic energy is transformed into enthalpy by the friction process. Determine the final condition of the H_2O leaving the guide vanes.

From the Mollier diagram, Chart A, Appendix, or by computation,

$$H_A - H_B = 1053.4 - 1040.3 = 13.1 \text{ Btu}$$

Substituting in Eq. (3)

$$[w_2^2 - (1 - 0.10)\overline{1{,}000}^2]/64.4 = 13.1 \times 778 \text{ ft-lb}$$

$$w_2 = \sqrt{13.1 \times 778 \times 64.4 + 900{,}000}$$

$$= 1{,}248 \text{ ft/sec}$$

Also,

$$H_{B'} = H_B + \eta(w_1^2/2g)$$

$$= 1040.3 \text{ Btu} + (0.10 \times 1{,}\overline{000}^2)/(64.4 \times 778)$$

$$= 1043.3 \text{ Btu}$$

From the Mollier diagram at a pressure of 12 lb/in.^{2} abs and $H = 1042.3$, $x = 0.893$.

The path followed on the *H-S* diagram for the diffuser process in the ideal case would be *AB* (Fig. 138). Friction causes the path to move to the right, resulting in the path *AB′*. Both diffuser processes illustrated have the same increase in enthalpy and consequently must have the same decrease in velocity according to Eq. (1). However, the friction effect reduces the pressure rise.

The effect of friction is indicated usually by the ratio of the adiabatic reversible increase in enthalpy, for the pressure rise, compared to the actual increase in enthalpy. This is commonly termed the *adiabatic efficiency*. This efficiency ranges from 0.70 to 0.90 depending on flow conditions and design of passage between the blades. The passages between the blades are short and curved in axial-flow compressors. Diffusers for centrifugal compressors are usually slightly curved or straight passages of appreciable length.

Example.—Air at 14.7 lb/in.^{2} and a temperature of 60 F enters the first row of stationary blades at a velocity of 800 ft/sec and leaves at a velocity of 200 ft/sec. The adiabatic efficiency is 0.80. Determine the pressure and temperature of the air leaving the blades.

Substituting in Eq. (1)

$$H_2 - H_1 = (\overline{800}^2 - \overline{200}^2)/(2 \times 32.2 \times 778) = 11.98 \text{ Btu/lb}$$

$$(\Delta H)_s = 0.80 \times 11.98 = 9.58 \text{ Btu/lb}$$

From Table XIX, Appendix, $(H_2)_s + (\Delta H)_s = 1033 + 9.58 \times 28.97 = 1310$ Btu/mole
and $(T_2)_s = 560°\text{R}$

From Eq. (10), page 242, and Table XXII, Appendix,

$$R \ln (P_2/P_1) = \int_{T_1}^{T_2} c_p \, dT/T = 0.52$$

Solving, $P_2 = 1.30 \times 14.7 = 19.1$ lb/in.
Also, $H_2 = H_1 + \Delta H = 1033 + 11.98 \times 28.97 = 1380$ Btu/mole
and $T_2 = 570°\text{R}$

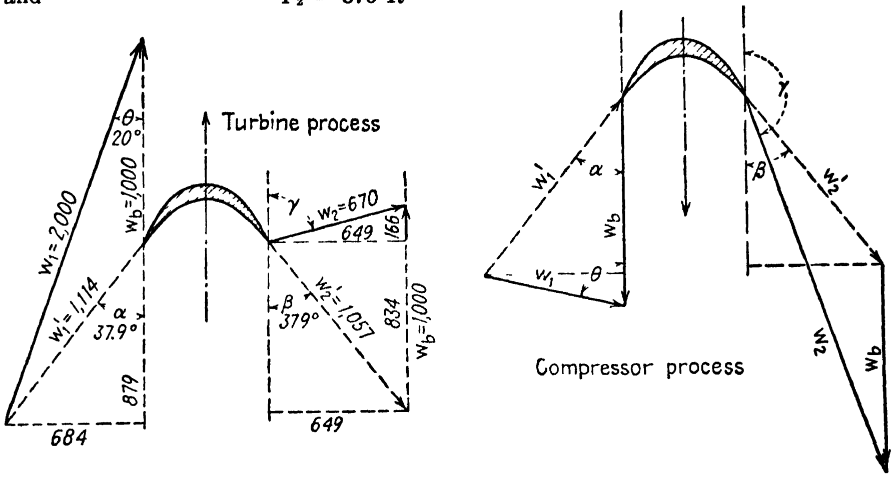

FIG. 139.—Velocity diagram for flow over moving blade (no pressure change).

Moving Blades; No Pressure Change.—Moving blades between which the fluid undergoes no pressure change are usually termed *velocity* or *impulse* blading. The fluid should approach the blade in a direction tangential to the surface of the blade over which the fluid is to flow. Otherwise, shock and turbulence of the jet result. These are friction processes and the work effect is reduced in the case of the turbine and increased in the case of the compressor.

The desired blade entrance angle is determined by the approaching fluid velocity and direction as well as the blade velocity. The fluid leaves a nozzle or stationary blades and is directed at the moving blades with a velocity of w_1 relative to the nozzle or stationary blades, and at an angle of θ (Fig. 139) from the plane of rotation of the blade. A combination of w_1 with w_b, the peripheral velocity of the blade, results in w_1', the velocity of the fluid relative to the moving blade. The angle α which w_1' makes with the plane of blade rotation is the desired entrance angle for the blade.

The fluid flows over the moving blade and because of fluid friction has its velocity reduced to w_2' relative to the blade. It leaves the blade with this relative velocity at an angle β with the plane of rotation, which is the exit angle of the blade. A combination of the relative exit velocity w_2' with the blade peripheral velocity w_b results in the exit velocity w_2 relative to the stationary parts of the machine.

The application of the Energy Equation to the process when viewed from a position on or relative to the moving blade is exactly the same as if the blade were stationary. No work is done when viewed from the moving blade and

$$KE_1' + H_1 = KE_2' + H_2 \tag{1}$$

in which $H_2 - H_1$ represents the increase in enthalpy at constant pressure because of friction reducing the fluid velocity.

When analyzed from a position on or relative to the stationary parts of a turbine, the Energy Equation becomes

$$KE_1 + H_1 = KE_2 + H_2 + W_{\text{out}} \tag{2}$$

and for the compressor

$$KE_1 + H_1 + W_{\text{in}} = KE_2 + H_2 \tag{3}$$

In both cases $H_2 - H_1$ is the same as in (Eq. 1). Also without friction the work in both cases is equivalent to the change in kinetic energy.

The force exerted by the fluid flowing over a moving blade is determined in the same manner as for the stationary blade. However, the absolute rather than the relative velocities or velocity components may be used. Thus, from Fig. 139,

$$\text{Force} = w_1' \cos \alpha - w_2' \cos \beta \tag{4}$$

$$= w_1 \cos \theta - w_2 \cos \gamma \tag{5}$$

The work per second per unit quantity of fluid flowing over the moving blade will be

$$\text{Work} = \text{force} \times \text{distance} = (w_1 \cos \theta - w_2 \cos \gamma)w_b/32.2 \tag{6}$$

Example.—Steam flows from a nozzle with a velocity of 2,000 ft/sec at an angle of 20 deg with the plane of rotation. The turbine blade has the same entrance and exit angles, and is moving with a peripheral velocity of 1,000 ft/sec. Determine the work done per pound of steam per second, and the condition of the steam as it leaves the blade.

Ten per cent of the initial kinetic energy relative to the blade is transformed into enthalpy by the friction of the water vapor in passing over the blade.

$$w_1 \cos\theta = 2{,}000 \cos 20 \text{ deg} = 1{,}879 \text{ ft/sec}$$
$$w_1 \sin\theta = 2{,}000 \sin 20 \text{ deg} = 684 \text{ ft/sec}$$

Referring to Fig. 139,

$$w_1' = \sqrt{(1{,}879 - 1{,}000)^2 + \overline{684}^2} = 1{,}114 \text{ ft/sec}$$

$$\alpha = \tan^{-1}\frac{684}{879} = 37.9 \text{ deg}$$

$$\overline{w_2'}^2/2g = (1 - y)\overline{w_1'}^2/2g = (1 - 0.10)\overline{1114}^2/2g$$

or

$$w_2' = 1{,}057 \text{ ft/sec}$$

$$w_2' \cos\beta = 1{,}057 \cos 37.9 \text{ deg} = 834 \text{ ft/sec}$$

$$w_2' \sin\beta = 1{,}057 \sin 37.9 \text{ deg} = 649 \text{ ft/sec}$$

$$w_2 = \sqrt{\overline{649}^2 + \overline{166}^2} = 670 \text{ ft/sec}$$

$$\text{Work} = (w_1 \cos\theta - w_2 \cos\gamma)w_b/32.2 = (1{,}879 - 166) \times 1{,}000/32.2$$
$$= 53{,}200 \text{ ft-lb} = 68.1 \text{ Btu/(lb/sec)}$$

Substituting in Eq. (2),

$$H_2 - H_1 = (w_1^2 - w_2^2)/2g - W_{\text{out}}$$
$$= (\overline{2{,}000}^2 - \overline{670}^2)/64.4 - 53{,}200 = 1940 \text{ ft-lb} = 2.5 \text{ Btu}$$

The value of H_2 will be 2.5 Btu higher than H_1 and at the same pressure.

Moving Blades; Pressure Change.—Moving blades when viewed from a position on them appear to be stationary. Hence, the analysis for this case is the same as for stationary blades with the fluid undergoing pressure change. The thermodynamic condition (P and H) of the medium as it approaches the moving blades is the same regardless of the position of the observer. The velocity of the fluid relative to the moving blades can be obtained as indicated in the case of the moving blades with no pressure change.

Usually the pressure decreases in turbine blades and increases in compressor blades.

The flow in this and the foregoing sections has been assumed to be axial, *i.e.*, each element of fluid contacts a given portion of the blade which is presumably at a given radius and consequently moving at a given peripheral velocity. Viewed from a position on a blade on the rotor of a centrifugal compressor, the change in peripheral velocity as the fluid flows radially is not observable but must be considered. In flowing outwardly from the axis of rotation to the periphery of a rotor with radial blades (Fig. 140), the fluid is accelerated from zero to the peripheral velocity when viewed from a stationary position. However, relative to the periphery of the rotor, the air is being decelerated from rotor peripheral velocity to zero velocity in a tangential direction while flowing radially outward. Thus, the air is compressed against the blade as it flows outwardly through the rotor of the centrifugal compressor and the pressure of the air increases to that corresponding to the decrease in air velocity relative to the moving blade.

Example.—Determine the pressure of the air as it leaves a centrifugal rotor with radial blades. The tip peripheral velocity is 1,000 ft/sec. The air enters the rotor at a pressure of 14.5 lb/in.^{2} abs and a temperature of 60 F.

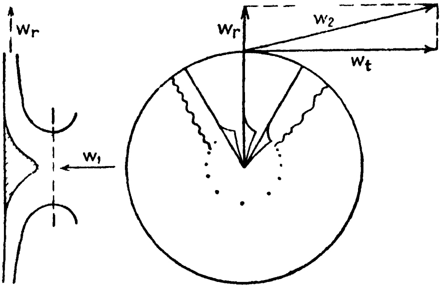

FIG. 140.—Sketch of rotor for centrifugal compressor.

The Energy Equation for this process is

$$H_1 = KE_2 + H_2$$

assuming that the entrance velocity is negligible. Then,

$$KE_2 = \overline{1{,}000}^2/(64.4 \times 778) = 19.96 \text{ Btu/(lb} \times \text{sec)}$$

This is the increase in H for the process. Inspection of the data in Table XIX, Appendix, or the use of the specific heat of air indicates a temperature rise of 83 F corresponding to this increase in H.

From Table XXII, Appendix, values for $\int c_p dT/T$ at 520 and 603°R are 0 and 1 033, respectively. Assuming that the compression is reversible, $S_1 = S_2$ and consequently

$$R \ln P_2/P_1 = 1.033 \qquad \text{See Eq. (10), p. 242.}$$

or

$$P_2 = 1.682 \times 14.5 = 24.4 \text{ lb/in.}^2 \text{ abs}$$

Deviations from the reversible process would result in a lower final pressure in practice.

FLOW THROUGH TURBINES

Velocity or Impulse Turbines.—The simplest type of turbine consists of one or more nozzles mounted on a rotating disk and discharging a fluid tangentially and opposite to the direction of disk rotation (Hero's reaction turbine). The optimum peripheral speed for this device is theoretically the discharge velocity from the nozzles since the final kinetic energy of the fluid is zero relative to the stationary parts of the turbine. If blades are mounted on the periphery of a rotating disk and the fluid is discharged through stationary nozzles tangentially toward the blades (Pelton water wheel), the optimum blade speed is theoretically one-half the nozzle discharge velocity if the blades reverse the direction of fluid flow.

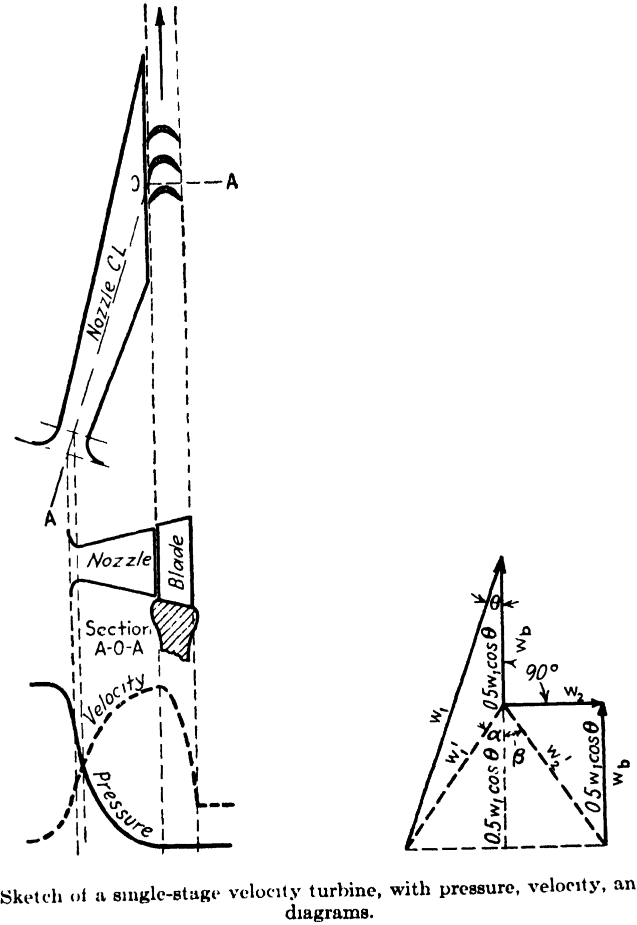

FIG. 141.—Sketch of a single-stage velocity turbine, with pressure, velocity, and ideal vector diagrams.

Single-stage *velocity* or *impulse* turbines usually have the nozzle axis inclined at a small angle (15 to 25 deg) to the plane of blade rotation. All of the pressure drop occurs in the nozzle and none in the blades. The fluid velocity increases in the nozzle and decreases in the blades (Fig. 141). The blades do not run full of the medium but have the medium flowing through them when in line with the jet issuing from the nozzle. The blades must be sufficiently long in a radial direction to extend beyond the projection of the nozzle.

The optimum peripheral blade speed, which results in the maximum work, is obviously somewhere between zero speed, at which the force on the blades does not act through any distance, and a speed of $w_1 \cos \theta$ (Fig. 141) at which the fluid does not produce a force on the blades. The expression for work, Eq. (6), page 264,

$$W = (w_1 \cos \theta - w_2 \cos \gamma) w_b / g \tag{1}$$

But, from Fig. 139,
$$w_2 \cos \gamma = w_b - w_2' \cos \beta \tag{2}$$

and
$$w_2' = w_1' \sqrt{1 - y} \tag{3}$$

hence,
$$w_2' \cos \beta = w_1' x \cos \alpha \sqrt{1 - y} \tag{4}$$

where x is the ratio of $\cos \beta / \cos \alpha$, if blade angles are unequal.

Also,
$$w_1' \cos \alpha = w_1 \cos \theta - w_b \tag{5}$$

hence,
$$w_2' \cos \beta = x \sqrt{1 - y}(w_1 \cos \theta - w_b) \tag{6}$$

and finally
$$W = (w_b w_1 \cos \theta - w_b^2)(1 + x\sqrt{1 - y})/g \tag{7}$$

Differentiating,
$$dW/dw_b = (w_1 \cos \theta - 2w_b)(1 + x\sqrt{1 - y})/g \tag{8}$$

and, for maximum work,
$$w_b = 0.5\, w_1 \cos \theta \tag{9}$$

which is the optimum peripheral speed for the single-stage velocity or impulse turbine regardless of exit-blade angle and friction effect. Obviously, decreasing the exit blade angle and also the friction increases the force on the blades, and consequently increases the work obtained from the turbine. Without friction and with equal blade angles, the direction of the absolute leaving velocity is axial (Fig. 141).

A single-stage velocity or impulse turbine must necessarily run at high peripheral and rotative speeds. Reduction in speed is accomplished by transforming the fluid kinetic energy into work in more than one stage of velocity blading. This is known as *velocity compounding.* Reducing the velocity of the fluid with two sets of moving blades requires a stationary set of guide vanes (Fig. 142) to direct the fluid in the desired direction toward the second set of moving blades.

The optimum peripheral blade speed for the two-stage velocity turbine may be determined in the same manner as for the single-stage machine. If x_1, x_2, and x_3 represent the ratios of the cosines of the leaving and entering angles of the first, second, and third set of blades, respectively, and y_1, y_2, and y_3, the friction factors for the three sets of blades, respectively, and A, B, and C represent the three $x\sqrt{1-y}$ terms, respectively, it can be shown that

$$w_b = \left(\frac{1 + A + AB + ABC}{2 + A + B + AB + BC + ABC + C}\right)\frac{1}{2}\, w_1 \cos\theta \qquad (10)$$

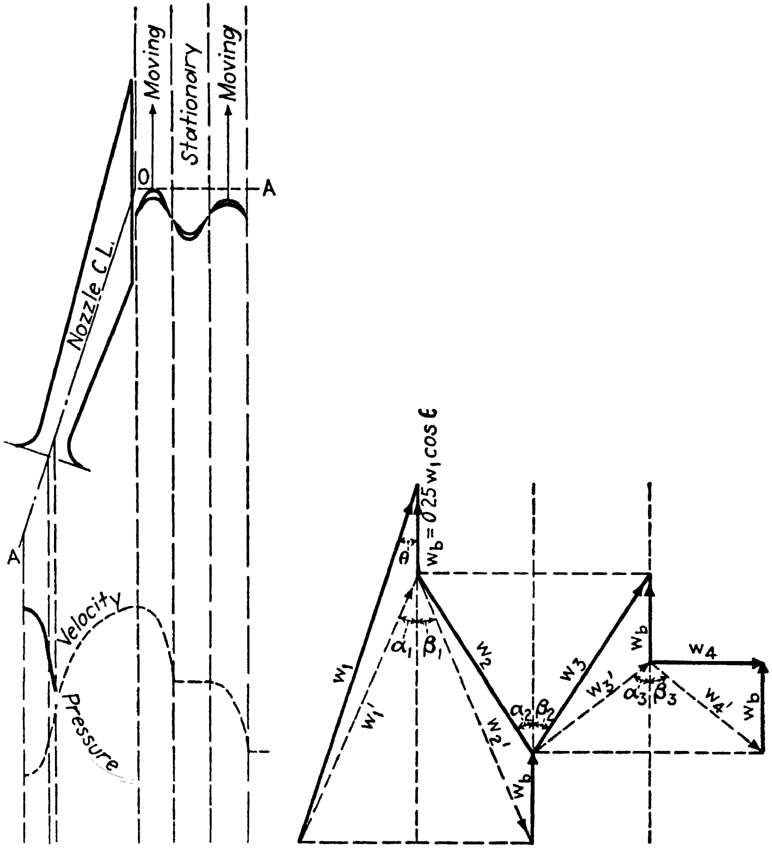

FIG. 142.—Sketch of a two-stage velocity-compounding turbine, with pressure, velocity, and ideal vector diagrams.

For the ideal case of no friction, y is zero. Also for equal entrance and exit angles, x is unity. For these conditions A, B, and C are unity and

$$w_b = 0.25\, w_1 \cos\theta \qquad (11)$$

The vector diagram for the ideal case with entrance and exit blade angles equal (Fig. 142) results in the final velocity, w_4, having no component in the plane of blade rotation. The work obtained from the first set of moving blades is three times that obtained from the second set.

For the same values of $x\sqrt{1 - y}$ for each set of blades, the optimum velocity is slightly lower than that indicated by Eq. (11).

A three-stage velocity turbine would permit the use of peripheral speeds one-third lower than for the two-stage turbine. However, the amount of work obtained from the third stage in the ideal case, with the entrance angle equal to leaving angle for each blade, is one-ninth of the total work. Consequently, other methods are ordinarily used for reducing the blade speed.

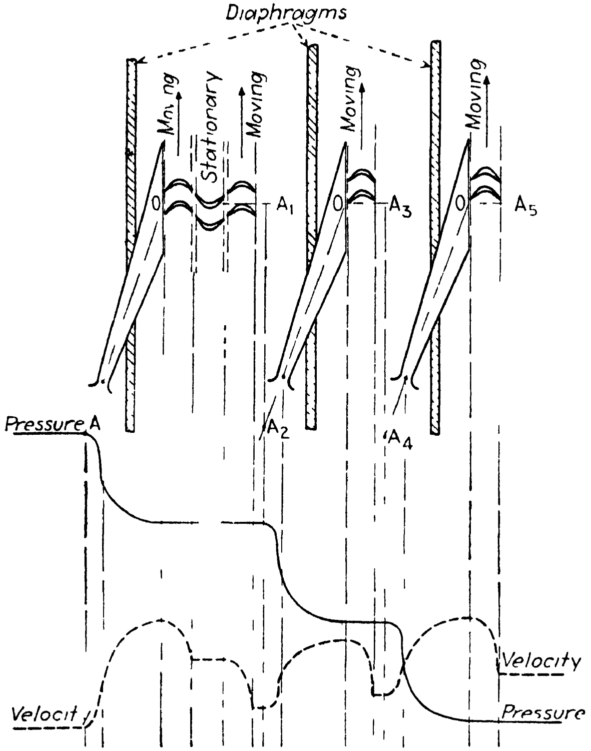

FIG. 143.—Velocity turbine with three pressure stages (pressure and velocity taken along $AOA_1A_2OA_3A_4OA_5$).

Pressure Compounding of Velocity or Impulse Turbines.—The blade speed may be reduced further by dividing the total pressure drop into a number of pressure stages, each stage consisting of a nozzle or set of nozzles and one or more rows of velocity blades. The pressure decreases in the nozzles only, while the velocity increases in the nozzles and decreases only in the moving blades in the ideal case (Fig. 143). Each pressure stage is separated from the others by diaphragms.

The blade velocity of any pressure stage is a function of the velocity of the fluid issuing from the nozzle. Neglecting the initial KE, the fluid velocity is a function of the $\sqrt{\Delta H}$ in the nozzle. Hence dividing the total ΔH through the turbine into N stages with equal ΔH changes reduces the blade velocity to $\sqrt{N}$ times the ideal velocity for a single-stage turbine, provided each pressure stage is a single-stage velocity turbine.

This type of turbine usually has two rows of velocity blades in the first pressure stage and one in each of the other stages. In most cases the nozzles are not of the type shown in the diagrammatic sketches but are the passages between a group or groups of curved guide vanes which permit nearly axial flow entering the nozzles, the curvature providing the desired velocity direction for the fluid leaving the nozzle blocks. The flow through the various nozzles and over the various moving and stationary blades is analyzed in the same manner as outlined in the previous section.

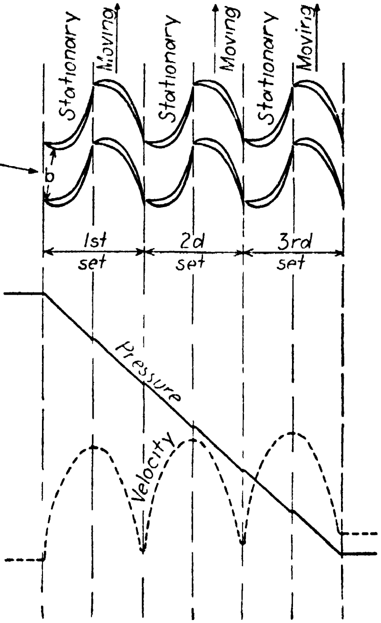

FIG. 144.—Pressure turbine blading (three sets of blades).

Pressure or Reaction Turbines.—This type of turbine consists of many sets of stationary and moving blades. There is a continuous pressure drop through all the blades of the turbine. This results in an increase of velocity in the stationary blades and a decrease in velocity in the moving blades (Fig. 144) when viewed from the stationary parts of the turbine. The blades are not symmetrical, usually having smaller exit than entrance angles. The blades run full of fluid, the length being computed to provide sufficient area for the flow of the fluid. The clearance between the moving blades and the turbine stator, and between the guide vanes and the rotor, must be quite small to reduce leakage past the ends of the blades to a minimum.

Example.—There are 301 blades in a row of stationary blades in a pressure turbine. The width b (Fig. 144) of the passage between the blades, perpendicular to the entering velocity, is 1 in. The velocity is 500 ft/sec. The quantity of fluid flowing is 50 lb/sec, and its specific volume is 125 ft^3/lb.

$$\text{Lb/sec} = \frac{\text{area} \times \text{velocity}}{\text{spec vol}} = \frac{(\text{blades} - 1)(b \times h) \times w_1'}{\text{spec vol}}$$

where h is the length of the blades and w_1' is the fluid velocity.

Hence
$$h = \frac{\text{lb/sec} \times \text{sp vol}}{(\text{blades} - 1)(b \div 12) \times w_1'}$$

Substituting the given values

$$h = \frac{50\ \text{lb/sec} \times 125\ \text{ft}^3/\text{lb}}{(301 - 1)(1 \div 12)\ \text{ft} \times 500\ \text{ft/sec}} = 0.5\ \text{ft} = 6\ \text{in.}$$

This is the radial length of the leading edge of the set of blades in question.

Combination Turbines.—The blades of the pressure or reaction turbine at the high-pressure end are comparatively short. Hence, the clearance between the ends of the stationary blades and the rotor, and between the ends of the moving blades and the stator, is an appreciable amount compared to the length of the blades, and appreciable fluid leakage occurs past the ends of the blades. However, at the low-pressure end of the pressure turbine the blades are long and leakage is a comparatively negligible factor. Consequently, in one type of turbine a velocity or impulse turbine is used for the high-pressure end and a pressure or reaction turbine for the low-pressure end. This is known as a *combination turbine* (Fig. 145) since both turbines are on the same shaft and in the same casing.

The high-pressure end of a combination turbine is usually a single-pressure stage with two stages of velocity compounding, having one set of nozzles and two rows of moving blades with a row of guide vanes between the moving blades. Usually half or more of the total pressure drop across the turbine occurs in this part of the turbine.

The medium discharged from this part of the turbine enters the low-pressure end of the turbine which consists of 10 to 30 sets of pressure blades through which the pressure drops gradually to the turbine back pressure.

Twisted Blades.—The distance from the center of rotation and the speed of rotation determine the blade speed, which is usually taken at the center line of the blades, *i.e.*, halfway between the tip and base of the blade. However, the tip of the blade has a higher velocity than the base because of the differences in radii. This necessitates larger entrance angles at the tip than at the base of the blades, which results in the twisted blade. It is customary to give this twist to the longer blades only, although all blades should have the twist for optimum results.

FLOW THROUGH COMPRESSORS

Axial-flow Compressors.—Axial-flow compressors may be designed with or without pressure change of the medium in the moving blades. However, by designing for a pressure increase in both stationary and moving blades, the mean fluid velocity may be kept reasonably low and high efficiencies may be attained. Thus, a set of stationary and moving blades (Fig. 146) has pressure and velocity effects the reverse of those for a set of blades for a pressure turbine (Fig. 144), *i.e.*, pressure rises in both blades and velocity decreases in the stationary and increases in the moving blades of the compressor. Relative to the blades, the velocity decreases in both the moving and the stationary blades. The blades may be designed so that the axial components of the various velocities are constant or varied as flow progresses through the turbine.

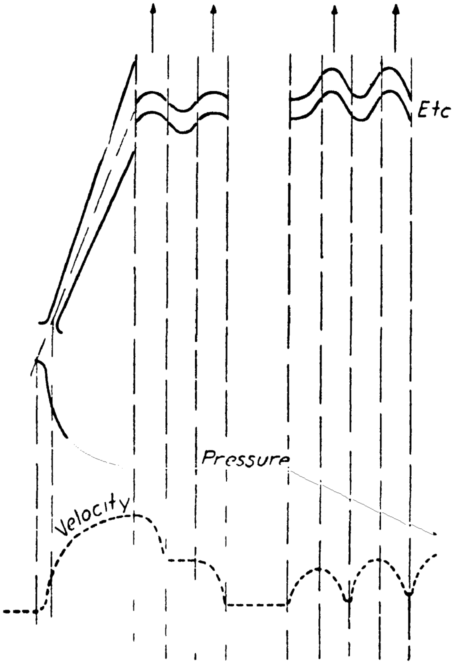

FIG. 145.—Combination turbine.

The number of sets of blades required is determined from the total pressure ratio desired and that obtainable from each set of blades.

Efficiencies under optimum operating conditions usually range from below 0.80 to above 0.90 depending on the excellence of design and number of stages.

Centrifugal Compressors.—A single-stage centrifugal compressor consists of a rotor with blades between which the air flows and is compressed while having its absolute velocity increased. The fluid is discharged into a diffuser which reduces the kinetic energy of the fluid and causes a further rise in pressure. These effects are both similar to those occurring with a set of blades for an axial compressor. See the section on Moving Blades with Pressure Change for further discussion of the process in the rotor.

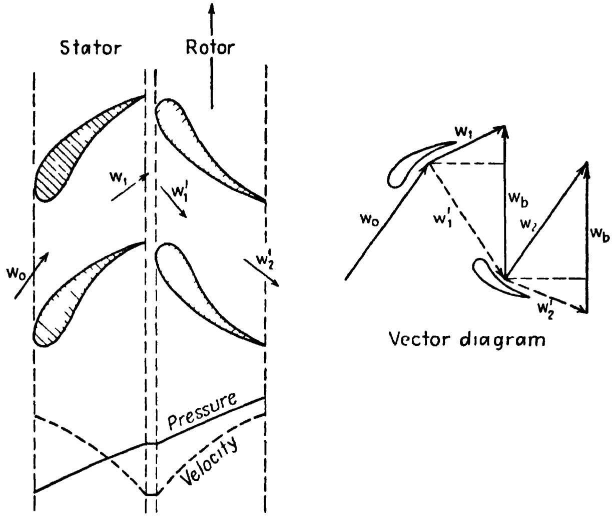

FIG. 146.—Sketch of one set of stationary and moving blades, pressure, velocity, and vector diagrams for an axial compressor.

Example.—Assuming a comparatively low radial velocity for the air flowing through the rotor in the example on page 266, determine the ideal pressure at the diffuser outlet

The low radial velocity (Fig. 140) indicates a final velocity (w_2 leaving the rotor) of not much more than the tip peripheral velocity. Thus, the temperature rise in the diffuser would be practically 83 F also.

From Table XXII, Appendix, $\int c_p dT/T$ at 686°R is 1.94. Then,

$$R \ln P_3/P_1 = 1.94$$

or

$$P_3 = 2.656 \times 14.5 = 38.5 \text{ lb/in.}^2 \text{ abs}$$

The pressure ratio in the diffuser is 6 per cent less than that in the rotor of the compressor for this case. The effect of the radial component of the air velocity leaving the rotor is to increase the pressure rise in the diffuser.

FLOW THROUGH PIPE LINES

Analysis of Fluid Flow.—Fluids flow through pipe lines when differences in pressure or potential energy exist between two sections of the line. The change in specific volume because of pressure change between sections is negligible in the case of mediums in the liquid state, but may be very appreciable in the case of mediums in the vapor or gaseous states. The flow of liquids is usually described as *incompressible* flow, while that of gases or vapors is termed *compressible* flow.

The expansion of mediums during flow results in an increase of kinetic energy and a decrease in temperature since the enthalpy decreases with an increase in kinetic energy. The fluid rubs against the pipe walls and dissipates some of its kinetic energy by the friction process. Also, the various strata or layers of the flowing fluid move with different velocities, exerting shearing forces on adjacent strata, and dissipate some of the kinetic energy by fluid friction. The result of both the friction on the pipe walls and the internal fluid friction tends to raise the temperature and increase the internal energy and enthalpy of the medium.

Heat flows in or out of the medium depending upon the temperature difference between the medium flowing through the pipe line and the medium around the outside of the pipe line. Thus, the effect of heat transfer in and the friction process is to reduce the decrease in temperature of a vapor or gas flowing through a pipe line which is surrounded by a medium at the same temperature as the initial temperature of the flowing medium.

Energy Dissipated by Friction.—The friction force that resists the flow of a small element, ΔM (Fig. 147), of a fluid under laminar flow conditions in a pipe line depends upon the area of contact with the pipe, the velocity of flow, and the density of the fluid in the element. Assuming that the friction force is directly proportional to each factor raised to some power,

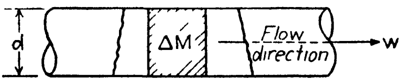

FIG. 147.—An element of fluid in a pipe line.

$$\text{Friction force} = f'(\text{density})^a(\text{velocity})^b(\text{rubbing surface})^c$$

or

$$\text{F.F.} = f'(\delta)^a(w)^b(A)^c \tag{1}$$

in which f' is a dimensionless coefficient of friction.

Substituting the dimensions in terms of mass (m), distance (l) and time (t), Eq. (1) becomes,

$$(mlt^{-2})^* = f(ml^{-3})^a(lt^{-1})^b(l^2)^c$$

The dimensions of both sides of this equation must be the same. Hence, the relation between the exponents on both sides of the equation must be as follows:

m terms, $1 = a$
l terms, $1 = -3a + b + 2c$
t terms, $-2 = -b$

---

* Mass × acceleration is substituted for the friction force.

Solving these equations simultaneously, $a = 1$, $b = 2$, and $c = 1$. Hence, the equation for the force of friction may be written as follows:

$$\text{F.F.} = f'\delta w^2 A = f''\delta\frac{w^2}{2g}\pi d\ \Delta L \tag{2}$$

where d is the diameter of the pipe and ΔL is the length of the fluid element, $\pi d\ \Delta L$ being the rubbing surface of the element (Fig. 147).

The length of the element depends upon the quantity of fluid in the element, its density, and the pipe diameter. Thus,

$$\Delta M = \Delta V \times \delta = \frac{\pi d^2}{4} \times \Delta L \times \delta$$

or

$$\Delta L = 4\ \Delta M\ \pi d^2\delta$$

Substituting this in Eq. (2), assuming a unit quantity of fluid,

$$\text{F.F.} = f''\frac{w^2}{2g}\frac{4}{d} \tag{3}$$

The work of friction when a given quantity of fluid flows past a given section is equal to the force of friction times the distance through which the force acts. Thus,

$$\Delta KE_f = f\frac{w^2}{2g}\frac{\Delta L}{d} \tag{4}$$

This is the well-known Darcy equation, ΔKE_f being equivalent to the friction head in feet, or potential energy loss because of friction

The Coefficient of Friction.—The relation for the coefficient of friction (Eq. 4) was developed for laminar flow. In this region f is a function of the Reynolds number only (Chart L, Appendix) for the usual pipe-line flow conditions. Above a value of Re of 2,000 the flow is usually turbulent. However, there is a *critical zone* extending from a minimum of $Re = 1{,}200$ to a maximum of $Re = 4{,}000$ in which the flow may be either laminar or turbulent depending upon the initial flow and pipe-line entrance conditions, changes of section, obstructions, etc.

Beyond the critical zone, there is a *transition zone* in which the coefficient f depends on both Re and a pipe surface roughness factor (e/d); beyond this is the *complete turbulence zone* in which the coefficient f depends only upon the surface roughness factor. The roughness factor and the coefficient of friction may be evaluated from Chart L, Appendix.

Flow of Liquids.—The specific volume and velocity of a liquid flowing through a pipe line remain constant. Hence Eq. (4) may be integrated between the limits 0 and L, the length of the pipe line, and the work of friction obtained per unit quantity of medium flowing through the pipe line. Thus,

$$KE_f = f\frac{w^2}{2g}\frac{L}{d} \tag{5}$$

Applying the Energy Equation to the medium in the pipe line between the entrance and the exit positions, assuming that the liquid temperature remains constant because of the heat transfer out of the medium being equal to the work of friction,

$$PE_1 + P_1V_1 = PE_2 + P_2V_2 + Q_{out} \tag{6}$$

For level pipe lines, or those in which the initial and final potential energies are the same, Eq. (6) becomes

$$V(P_1 - P_2) = f\frac{w^2}{2g}\frac{L}{d} \tag{7}$$

where v = specific volume, ft³/lb,
P = absolute pressure, lb/ft²,
and L = length of the pipe line, ft.

Example.—Determine the maximum velocity of flow and pressure drop per 1,000 ft of 3-in. steel pipe line required for laminar flow of crude oil having a specific gravity of 0.925. $Re = 2{,}000$ and pipe line temperature is 70 F.

From Chart K, Appendix, at 70 F, $\nu = 0.00070$.

The inside diameter of 3-in. standard pipe is 3.07 in. = 0.256 ft.

Then, $w = Re\nu/d = 2{,}000 \times 0.00070 \times 12/3.07 = 5.47$ ft/sec

From Chart L, Appendix, at $Re = 2{,}000$, $f = 0.032$.

Substituting in Eq. (7),

$$P_1 - P_2 = 0.032 \times \overline{5.47}^2 \times 1{,}000 \times 62.4 \times 0.925/(64.4 \times 0.256)$$
$$= 3{,}360 \text{ lb/ft}^2 = 23 \text{ lb/in.}^2$$

Example.—Determine the velocity of flow and pressure drop for the foregoing example for a value of $Re = 10{,}000$.

Obviously the velocity will be $5.47 \times 10{,}000/2{,}000 = 27.4$ ft/sec.

From Chart L, Appendix, for commerical steel pipe, the roughness factor is 0.00058.

From Chart L, at $Re = 10{,}000$ and $e/d = 0.00058$, $f = 0.0318$.

Substituting in Eq. (7),

$$P_1 - P_2 = 0.0318 \times \overline{27.4}^2 \times 1{,}000 \times 62.4 \times 0.925/(64.4 \times 0.256)$$
$$= 83{,}600 \text{ lb/ft}^2 = 581 \text{ lb/in.}^2$$

Flow of Vapors and Gases.—The flow of fluids in a pipe line results in friction and heat transfer. Thus, the general entropy equation is applicable. This is,

$$T\,\Delta S = KE_f + Q_{in} - Q_{out} \tag{8}$$

Flow through a pipe line of appreciable length may be assumed to result in an equilibrium condition for the medium at all points along the pipe line. Consequently, the path of the process, 1 to 2 (Fig. 148), may be plotted. Area C on each of the diagrams represents the same amount of energy.* Also, area A on the P-V diagram is equivalent to $H_1 - H_3$, and area $A + C$ is equivalent to $\int V\,dP$.

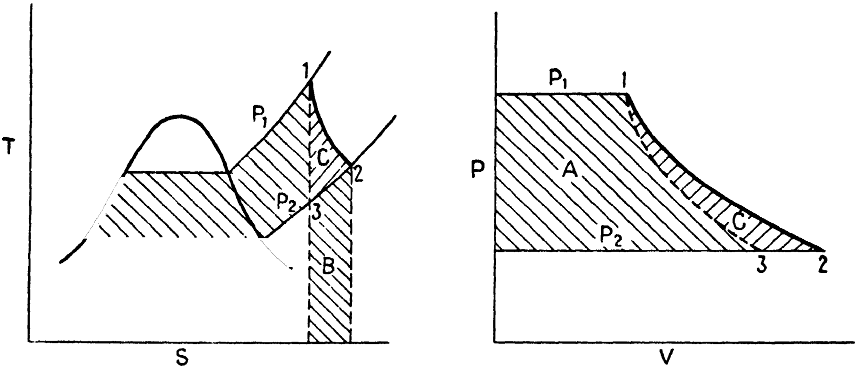

Fig. 148.—T-S and P-V diagrams for pipe-line processes.

Then, Eq. (8) may be written as follows:

$$\text{Area}(C + B)_{T\text{-}S\text{ diag}} = \text{area } C_{P\text{-}V\text{ diag}} + \text{area } B_{T\text{-}S\text{ diag}} = KE_f - \Delta Q \quad (9)$$

or
$$[-\int V\,dP - (H_1 - H_3)] + (H_2 - H_3) = KE_f - \Delta Q \quad (10)$$

or
$$\int V\,dP + (H_1 - H_2) + KE_f - \Delta Q = 0 \quad (11)$$

The Energy Equation for the pipe-line process is

$$H_1 - H_2 = KE_2 - KE_1 + \Delta Q \quad (12)$$

Combining Eqs. (11) and (12), results in

$$\int V\,dP + KE_f + \Delta KE = 0 \quad (13)$$

$$\Delta KE = \int d\frac{(w^2)}{2g} = \int \frac{w\,dw}{g} \quad (14)$$

Also, from Eq. (4),
$$KE_f = \int f\,\frac{w^2}{2gd}\,dL \quad (15)$$

Combining Eqs. (13) to (15), results in the general pipe-line equation,

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* This may be proved by assuming that the path 1 to 2 is a frictionless expansion in a turbine. Paths 2 to 3 and 3 to 1 complete a cycle enclosing area C on both the P-V and T-S diagrams. On the T-S diagram, area C represents the net heat added, and on the P-V diagram area C represents the net work. In a cycle these two values are equal. Hence, the areas represent the same amounts of energy.

$$\frac{g}{w^2} V\,dP + \frac{f}{2d}\,dL + \frac{dw}{w} = 0 \tag{16}$$

From the Continuity Equation and the Equation of State for perfect gases,

$$w^2 = M^2V^2/A^2 = M^2R^2T^2/A^2P^2$$

Hence, $$\frac{V}{w^2} = \frac{RT}{P} \times \frac{A^2P^2}{M^2R^2T^2} = \frac{A^2P}{M^2RT} = \frac{\pi^2 d^4 P}{16 m M^2 RT}$$ [*]

Substituting this value for V/w^2 in Eq. (16), and integrating with T constant, results in

$$\frac{d^4}{155.2 m M^2 T}(P_2^2 - P_1^2) + f\frac{L}{2d} + \frac{1}{2}\ln\frac{w_2}{w_1} = 0 \tag{17}$$

The term $0.5 \ln w_2/w_1$ will usually be negligible. Hence,

$$P_1^2 - P_2^2 = 77.6 f m M^2 LT/d^5 \tag{18}$$

Example.—Ten moles of air per minute are to be transported through a pipe line 1 mile in length. The air enters the pipe line at a pressure of 150 lb/in.^{2} abs and at a temperature of 60 F. The pressure at the end of the pipe line is to be not less than 130 lb/in.^{2} Determine the desirable pipe size, assuming an isothermal flow process.

At 60 F and a mean pressure of 140 lb/in.^{2} abs, the kinematic viscosity ν (Chart K, Appendix) is about 0.00002 ft^2/sec.

Also, $$V_{\text{mean}} = RT/P = 1{,}545 \times 520/(140 \times 144) = 399 \text{ ft}^3\text{/mole.}$$

Now, assuming a pipe diameter of 5 in.,

$$w = \frac{MV}{A} = \frac{10}{60} \times \frac{4 \times 144}{\pi\, 5^2} \times 399 = 48.7 \text{ ft/sec}$$

Then, $$\text{Reynolds no.} = wd/\nu = 18.7 \times 5/(12 \times 0.00002) = 1{,}013{,}000$$

From Chart L, Appendix, the roughness factor for 5-in. commercial steel pipe is 0.00035. At this roughness factor and the Reynolds number of 1,013,000 the friction factor f (Chart L) is 0.0160.

Substituting in Eq. (18) and solving for d,

$$d = \left[\frac{77.6 \times 0.0160 \times 28.97 \times (10/60)^2 \times 5{,}280 \times 520}{144^2(150^2 - 130^2)}\right]^{\frac{1}{5}} = 0.473 \text{ ft} = 5.68 \text{ in.}$$

Obviously 5-in. pipe is too small and 6-in. pipe having an internal diameter of 6.07 in., approximately, must be used. Solving again with this pipe diameter results in a final pressure of 136 lb/in.^{2} abs.

Short lines having small pressure drops usually have small changes in fluid velocity and specific volume. If these changes are assumed to be negligible, the integration of Eq. (16) results in

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[*] *m* is the molecular weight of the medium and, when introduced, changes the dimensions to a pound basis. Note that *MR* is the same on either a pound or mole basis, but that this in not true of M^2R.

$$V(P_1 - P_2) = f\frac{w^2}{2g}\frac{L}{d} \tag{19}$$

which is the same as Eq (7) which was derived for liquid flow.

Example.—Steam at a pressure of 250 lb/in.^{2} abs and 500 F is flowing through a 3-in. pipe line 100 ft long. The mean velocity of the steam is 100 ft/sec. Determine the quantity per hour and the pressure drop. Use extra-strong pipe.

The internal diameter of extra-strong 3-in. pipe is 2.90 in. The specific volume of the steam is 2.151 ft^3/lb, Table VIII, Appendix.

The quantity flowing per hour is

$$3{,}600 \times \frac{\pi \times \overline{2.90}^2}{4 \times 144} \times 100 \div 2.151 = 7{,}670 \text{ lb/hr}$$

From Chart L, Appendix, at 250 lb/in.^{2} and 500 F, the kinematic viscosity of steam is 0.000032 ft^2/sec, approximately.

$$\text{Reynolds no.} = wd/\nu = 100 \times 2.90/(12 \times 0.000032) = 755{,}000$$

The roughness factor for steel pipe 2.9 in. in diameter (Chart L) is 0.0006, and the friction factor f is 0.018.

Substituting in Eq. (19),

$$P_1 - P_2 = 0.018 \times \frac{100^2}{64.4} \times \frac{100 \times 12}{2.90} \times \frac{1}{2.151}$$
$$= 538 \text{ lb/ft}^2 = 3.7 \text{ lb/in.}^2$$

Frictionless Flow.—Very short pipes or ducts may be assumed to have little or no friction. In this case the second term in Eq. (16), page 279 is, eliminated, and

$$-dP = w\,dw/gV \tag{1}$$

From the Continuity Equation,

$$w/V = M/A \tag{2}$$

Thus, for constant area of pipe cross section and steady flow M/A is a constant and, consequently,

$$w_1/V_1 = w_2/V_2 = \text{const} \tag{3}$$

Integrating Eq. (1) results in

$$P_1 - P_2 = \frac{w}{gV}(w_2 - w_1) \tag{4}$$

$$= \rho_2 w_2^2 - \rho_1 w_1^2 \tag{5}$$

in which ρ is the mass density. This relation may be used for frictionless flow with heat transfer in or out of the medium while flowing through a very short pipe. Eq. (5) indicates the ideal pressure drop in a constant-area burner.

Experimental Evaluation of f.—The general relationship for the pipe-line process [Eq. (16) page 279],

$$\frac{g}{w^2} V\,dP + \frac{f}{2d}\,dL + \frac{dw}{w} = 0 \tag{1}$$

may be combined with the Continuity Equation

$$MV = Aw \tag{2}$$

to eliminate the velocity term w. This results in the expression

$$\int_1^2 \frac{dP}{V} + \frac{8M^2L}{\pi^2 d^5 g} f + \frac{M^2}{gA^2} \ln \frac{w_2}{w_1} \tag{3}$$

Pressure and temperature are determined experimentally at various sections along a pipe line between sections 1 and 2. These values indicate the specific volume of the medium at the various sections if the medium is superheated vapor or a gas. The weight rate of flow is determined experimentally. The first term in Eq. (3) may be evaluated by plotting $1/V$ vs. P and integrating between P_1 and P_2. The coefficient of f is evaluated from the flow rate and pipe-line dimensions. The third term is evaluated from the specific-volume, flow-rate, and pipe-line measurements. Thus, f can be evaluated by means of Eq. (3) with experimental data on pipe-line flow.

EXERCISES

1. Compute the theoretical and actual flow velocities, Mach numbers, and rates of flow of air through a well-rounded orifice having an area of 1 in.^{2} Initial conditions are 200 lb/in.^{2} abs, 100°R and a negligible velocity of approach. Use pressure ratios of P_2/P_1 of 0.2, 0.4, 0.6, and 0.8. Also compute the orifice areas for these pressure ratios for a flow rate of 1 mole of air per second. Plot the results as in Fig. 125.

2. Solve Exercise 1 for H_2O at an initial condition of 200 lb/in.^{2} abs and saturated.

3. Solve Exercises 1 and 2 for a ratio of pipe area ahead of the orifice to orifice area of 2 to 1.

4. Design a nozzle for steam with an initial pressure of 200 lb/in.^{2} abs and a temperature of 500 F. The back pressure is 1 lb/in.^{2} abs. The friction loss in the expanding section of the nozzle is 0.15 of the total ideal enthalpy drop. The nozzle is to discharge 1 lb of steam per second.

5. Determine the nozzle-throat and -exit area for a gas turbine. Initial air conditions are 60 lb/in.^{2} abs and 1800°R. Back pressure is 14.7 lb/in.^{2} abs. Friction loss in the diverging section of the nozzle is 0.10 of the total ideal enthalpy drop. Velocity of approach is 200 ft/sec. Compute the Mach numbers for the conditions at the throat and exit of the nozzle.

6. Plot a Fanno line passing through the point representing the condition of the steam in the nozzle in Exercise 4 when the pressure is 30 lb/in.^{2} abs, the friction loss at this point being 0.05 of the total enthalpy drop through the nozzle. Then determine the maximum possible shock pressure at this section of the nozzle.

7. Plot a Fanno line for the air condition at the exit of the nozzle in Exercise 5, and determine the maximum possible shock pressure at this section of the nozzle.

8. Determine the ideal entrance, throat, and exit areas of a ram chamber for a jet-propelled plane flying at a speed of 1,200 mph at an altitude of 40,000 ft. Air flow is 100 lb/sec. Assume a negligible exit velocity.

9. The air leaving the ram chamber in Exercise 8 is compressed adiabatically and reversibly to a pressure 5 times the ram pressure. Determine the ideal work requirement of the supercharger.

10. The compressed air in Exercise 9 passes through the jet burner and is heated to 2000°R. It then flows through an ideal turbine which drives the compressor. Determine the exit velocity of the gases and the net thrust of the jet engine. Compute the net thrust horsepower and estimate the specific fuel consumption and miles per gallon of dodecane.

11. The entering and leaving velocities of steam over stationary guide vanes are 1,000 and 950 ft/sec, respectively. Determine the value of y which is the part of the initial kinetic energy which is transformed by friction into enthalpy. No pressure drop occurs during the process.

12. Water vapor at 14.7 lb/in.^{2} abs pr and saturated enters a row of stationary guide vanes with a velocity of 1,000 ft/sec. The pressure drops to 12 lb/in.^{2} and the velocity increases to 1,200 ft/sec. Determine the part of the initial kinetic energy converted by friction into enthalpy, and the final condition of the vapor.

13. Assume that air is the medium in Exercise 11. Determine the temperature rise for the process.

14. Air enters the stationary blades of a compressor with a velocity of 500 ft/sec and leaves with a velocity of 400 ft/sec. Determine the pressure ratio and the temperature rise assuming the initial temperature is 100 F. The adiabatic efficiency is 0.85.

15. A fluid issues from a nozzle with a velocity of 2,000 ft/sec at an angle of 20 deg to the plane of blade rotation. The turbine blade has the same entrance and exit angles and is moving with the optimum peripheral velocity. Ten per cent of the initial kinetic energy relative to the blade is dissipated by friction. Determine the blade velocity, blade angles, and the work per pound of steam per second flowing over a row of such blades. No pressure drop occurs in the blades.

16. The moving blades of a compressor have equal entrance and exit angles of 30 deg. The blade speed is 1,000 ft/sec. The air is approaching the moving blades with an axial velocity direction.

a. Determine the desirable value for the absolute velocity of approach and absolute leaving velocity assuming a 10 per cent kinetic energy loss in flowing over the blade. The pressure is assumed to remain constant.

b. Also, determine the work done by the blades per pound of air per second flowing over the blades.

17. Water vapor at 14.7 lb/in.^{2} abs pr and $x = 0.96$ approaches a row of moving blades with a relative velocity of 1,200 ft/sec. The pressure drops to 10 lb/in.^{2} during flow over the blades. The blades have entrance and exit angles of 60 deg. The regenerative effect y is 0.10. The blades are moving with a peripheral velocity of 1,000 ft/sec. Determine the final condition of the vapor, its final velocity, and the work per pound of vapor per second flowing over the blade.

18. Assume that the air flowing over the moving blades in Exercise 16 has its velocity reduced to 0.5 of the relative entering velocity while the pressure is increased with an adiabatic efficiency of 0.85. Determine the pressure ratio and work required per pound of air per second flowing over the blades.

19. Make a preliminary design of a centrifugal compressor rotor and diffuser to have a pressure ratio of 2:1, and to compress 5,000 lb of air per hour. The air approaches the rotor at a pressure of 14.7 lb/in.^{2} abs and a temperature of 60 F, and with a velocity of 300 ft/sec.

20. Make a preliminary design of the first set of moving and stationary blades for an axial-flow compressor to compress the air in Exercise 19. The pressure ratio for the set of blades is 1.25 to 1.

21. A turbine is to operate between conditions of 250 lb/in.^{2} and 500 F, and 2 in. Hg abs pr. The turbine is to be of the velocity type with four stages of pressure compounding, the first pressure stage having two velocity stages while the others have each one row of velocity blades. Assume a regenerative effect across each blade of 0.07 of the entering relative *KE*, and of 0.10 of the *H* drop for each nozzle. Assume pressure drops for each pressure stage such that the peripheral velocity will be about the same. Determine the work per pound of steam per second, the ratio of the work to the ideal *H* drop, and plot the condition curve on an *H-S* diagram.

22. Determine the minimum size of pipe line and the pressure drop per 1,000 ft to transport 250 gal of oil per minute with viscous flow. The oil has a specific gravity of 0.92 and an absolute viscosity of 0.60 poise.

23. Compute the pressure, specific volume, and velocity of air for each mile length of pipe in the example on page 279 until the air pressure is 14.7 lb/in. Determine the actual length of pipe line, and plot the pressure, velocity, and specific weight against pipe-line length.

24. Air enters a 5-in. pipe with a velocity of 500 ft/sec. The pressure is 50 lb/in^2 abs and the temperature is 100 F. 7000 Btu are added to each mole of air. Determine the pressure, temperature, and velocity of the air leaving the pipe, assuming frictionless flow.

APPENDIX

THERMODYNAMIC RELATIONS AND PROPERTIES

THERMODYNAMIC RELATIONS

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THERMODYNAMIC RELATIONS AND PROPERTIES OF MEDIUMS

Tables of properties of mediums usually contain values for the coordinates P, V, and T, values for the energy properties U and H, and values for S. The latter three may also be used as coordinates, for they are functions of the state of the substance only.

The development of the various tables of data for the various mediums is dependent upon experimental data and thermodynamic relationships. The experimental data consist usually of the following:

1. Pressure-temperature data for saturated mediums.
2. Specific-volume data for saturated liquid, saturated vapor, and superheated vapor.
3. Specific heats for saturated liquid.
4. Specific heats for liquid and for superheated vapor, both at constant pressure.
5. Latent heats of vaporization.
6. Pressure-temperature data for throttling experiments with vapor.

Experimental results provide data for the formulation of equations of state between the coordinates P, V, and T.

Thermodynamics and mathematics provide relationships between the various coordinates and properties by means of which the experimental data may be checked for thermodynamic consistency.

Equations of State.—These are relations between the coordinates P, V, and T. Some of these equations are based on the Kinetic* Theory of Gases and others are purely empirical. The perfect-gas Equation of State

$$PV = RT \tag{1}$$

was first developed from experimental data and later derived from the Kinetic Theory of Gases. This equation is correct for gases at zero pressure but may be used for real gases with little error at low pressures or whenever the conditions are such that the internal energy or enthalpy of the medium is very nearly a function of the temperature (see page 53).

Many equations of state have been developed and used in the formulation of properties of mediums, but none satisfies the experimental data except for a limited range These equations range from the comparatively simple equation of van der Waals proposed in 1873,

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*Many relationships between the coordinates and properties of mediums may be developed. See BRIDGMAN, P. W., "A Condensed Collection of Thermodynamic Formulas," Harvard University Press, 1925.

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{2}$$

to complex relations such as that of Beattie and Bridgeman[*]

$$P = \frac{RT(1 - c/VT^3)}{V^2}\left[V + B_0\left(1 - \frac{b}{V}\right)\right] - \frac{A_0}{V^2}\left(1 - \frac{a}{V}\right) \tag{3}$$

The National Bureau of Standards developed the relation

$$V = \frac{AT}{P} - \left(\frac{B}{T^3} + \frac{C + DP}{T^{11}} + \frac{EP^5}{T^{19}}\right) - F + Tf_1(P) \tag{4}$$

for ammonia[†] vapor. All equations of state should satisfy certain criteria,[‡] one of which is that of approaching the perfect gas relation as P approaches zero.

Modern physics has added considerably to the knowledge of the forces between molecules that cause deviations from the perfect-gas equation. These forces are usually expressed in the form of an intermolecular potential energy, E, which is a

[*] Beattie, J. A., and O. C. Bridgeman, *Pro. Am. Acad. Arts Sci.*, **63**, 229–308 (1928).

[†] All equations for ammonia were obtained from the *Nat. Bur. Standards, Cir.* **142** (1923). The following table contains the data for these equations.

Constant	Equation number			
	(4)	(7)	(32)	(33)
A	0.6301952	2.55743247×10	7.60959×10	0.619546
B	3.18228×10^7	3.2951254×10^3	2.3577×10^7	1.7683×10^7
C	3.80226×10^{27}	6.4012471	8.451×10^{27}	7.747×10^{27}
D	2.29909×10^{26}	4.148279×10^{-4}	2.555×10^{26}	2.3421×10^{26}
E	1.1778×10^{38}	1.4759945×10^{-6}	7.272×10^{37}	6.908×10^{37}
F	0.041648	....	0.007714	0.2687723
G	....	....	0.269065	3.16094×10^{-4}
I	....	....	1.58047×10^{-4}	3.3048×10
K	....	....	2.62303×10^2	0.028463

$f_1(P) = (5300 - 32P + 0.10132P^2 - 0.0000992P^3)10^{-8}$.

$f_2(P) = -P(982 - 2.964P + 0.006255P^2 - 0.00000459P^3)10^{-8}$.

[‡] Dodge, B. F., "Chemical Engineering Thermodynamics," pp. 152–201, McGraw-Hill Book Company, Inc., New York, 1944.

function of the distance r between two molecules and can be calculated by means of the principles of quantum mechanics.

It is now customary to write the Equation of State of an actual gas as an expansion in inverse powers of the volume. Thus,

$$PV = RT\left(1 + \frac{B}{V} + \frac{C}{V^2} + \cdots\right) \qquad (a)$$

The coefficients 1, B, C, etc., are called *virial* coefficients. For sufficiently low pressures the series may be terminated after the second term, and B may be computed from the relation

$$B = 2\pi N \int_0^\infty \left(1 - e^{\frac{-E}{kT}}\right) r^2\, dr \qquad (b)$$

in which N is the number of molecules per mole of gas and k is the Boltzmann constant, R/N.

Van der Waals' equation may be expanded as follows:

$$PV = RT + Pb - \frac{a}{V} + \cdots \qquad (c)$$

and, if P is approximated by RT/V,

$$PV = RT\left(1 + \frac{b - a/RT}{V} + \cdots\right) \qquad (d)$$

From Eqs. (a) and (d), the second virial coefficient B, in Eq. (a), is

$$B = b - a/RT \qquad (e)$$

Equation (e) is in agreement with Eq. (b) if E varies with r as indicated in Fig. 149. In this illustration r_0 is the distance between molecules at which very strong repulsion and very high intermolecular potential energy are present.

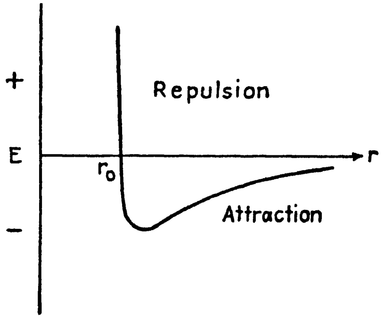

FIG. 149.—Variation of intermolecular potential energy with distance between molecules.

Since for $r < r_0$, $e^{\frac{-E}{RT}} = 0$, Eq. (b) becomes

$$B = 2\pi N \int_0^{r_0} r^2\, dr + 2\pi N \int_{r_0}^\infty \left(1 - e^{\frac{-E}{kT}}\right) r^2\, dr \qquad (f)$$

Also, for sufficiently high temperatures (ordinary conditions), $E << kT$, and the second integrand is Er^2/kT. Hence,

$$B = \frac{2}{3}\pi N r_0^3 + \frac{2\pi N}{kT} \int_{r_0}^\infty Er^2\, dr \qquad (g)$$

Comparing Eqs. (e) and (g),

Van der Waals' $b = 2\pi N r_0^3/3$, from which r_0 may be computed if b is known. Also,

Van der Waals' $a = -2\pi N^2 \int_{r_0}^\infty Er^2\, dr$, from which E may be evaluated if a is known.

The perfect-gas equation is used extensively for the evaluation of the properties of mediums by introducing the *compressibility factor Z*. Thus

$$PV = ZRT \tag{5}$$

The compressibility factor is evaluated from experimental determinations of the specific volume at various pressures and temperatures (see Table XXIII, Appendix). A plot of the compressibility factor vs. pressure for various temperatures indicates the effect of pressure and temperature on deviations from the perfect-gas state (see Charts F and G, Appendix). The use of reduced coordinates (page 59) provides the generalized charts referred to, which may be used for evaluating coordinates and properties with a fair degree of accuracy if only the critical conditions are known.

The deviation from the perfect-gas relationship is also indicated by the residual volume (Chart E, Appendix) which is defined as

$$r = RT/P - V = (1 - Z)\,RT/P \tag{6}$$

The relation between P and T for the saturated condition is usually of the form

$$\log_{10} P = A - B/T - C \log_{10} T - DT + ET^2 \qquad (7)^*$$

which was developed for ammonia.

Relations between P, V, T, and S (Maxwell Relations).—The Energy Equation for a nonflow process without chemical reaction is

$$\Delta U + \Delta W + \Delta Q = 0 \tag{8}$$

in which $\Delta U = U_2 - U_1$,
$\Delta W = W_{\text{out}} - W_{\text{in}}$,
and $\Delta Q = Q_{\text{out}} - Q_{\text{in}}$.

For an increment of change, Eq. (8) may be written

$$dU + dW + dQ = 0 \tag{9}$$

The entropy equation for a reversible process of increment change is

$$dS = -dQ/T \tag{10}$$

The definition of enthalpy provides the relationship

$$H = U + PV \tag{11}$$

which is useful for constant-pressure processes. Thus, holding P constant,

$$dH = dU + P\,dV = -dQ \tag{12}$$

Two other relations between coordinates and properties have been developed and found useful for constant-temperature processes. These are

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* *Ibid.*, p. 288.

$$F_V = U - TS \tag{13}$$

and

$$F_P = H - TS \tag{14}$$

Differentiating Eq. (13), holding T constant,

$$dF_V = dU - T\,dS = -dW_V \tag{15}$$

in which dU and dW_V are increments of energy in the most comprehensive sense, *i.e.*, including chemical energy, electrical energy, work, etc.

Differentiating Eq. (14), holding both T and P constant,

$$dF_P = dU + P\,dV - T\,dS = -dW_V + P\,dV = -dW_P \tag{16}$$

The term *free energy* has been applied to both functions F_V and F_P, but is now used almost exclusively for the latter function. The former is termed the Helmholtz function and the latter the Gibbs function. Equations (15) and (16) indicate that chemical equilibrium will be attained in a reaction process when F is a minimum since the work of reaction will then be a maximum. If a system is not in equilibrium, there is a possibility for a spontaneous change and this possibility is indicated by the difference between the F values of the system in its given condition and at the condition at the end of the assumed spontaneous change.

Obvious combinations of Eqs. (9) to (14), result in the following relationships:

$$dU = T\,dS - P\,dV \tag{17}$$

$$dH = T\,dS + V\,dP \tag{18}$$

$$dF_V = -S\,dT - P\,dV \tag{19}$$

$$dF_P = -S\,dT + V\,dP \tag{20}$$

Applying Eq. (17) to a constant-volume process results in

$$\left(\frac{\delta U}{\delta S}\right)_V = T \tag{21}$$

Likewise, Eq. (18), for a constant-pressure process becomes

$$\left(\frac{\delta H}{\delta S}\right)_P = T \tag{22}$$

The last relationship may be used to check the consistency of the data given for H, S, and T.

Example.—Check the consistency of the Keenan and Keyes steam tables at a pressure of 100 lb/in. abs and a temperature of 540 F

This may be done approximately by determining ΔH and ΔS for the range of temperature from 520 to 560 F. Thus,

T	H	S
560	1309.1	1.7389
520	1289 2	1.7189
Difference...	19.9	0 0200

$$\left(\frac{\Delta H}{\Delta S}\right)_P = \frac{19.9}{0.02} = 995°\text{R} = 535 \text{ F}$$

The slope of the 100-lb pressure line at 540 F on the H-S diagram will provide a more accurate check.

The properties U, H, F_V, and F_P are functions of the state only, and consequently, (Eqs. (17) to (20) are exact differentials. The application of the test for exact differentials* to these equations results in the following *Maxwell* relations:

$$\left(\frac{\delta T}{\delta V}\right)_S = -\left(\frac{\delta P}{\delta S}\right)_V \tag{23}$$

$$\left(\frac{\delta T}{\delta P}\right)_S = \left(\frac{\delta V}{\delta S}\right)_P \tag{24}$$

$$\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V \tag{25}$$

$$\left(\frac{\delta S}{\delta P}\right)_T = -\left(\frac{\delta V}{\delta T}\right)_P \tag{26}$$

Example.—Equation (26) indicates that if volume passes through a minimum with temperature change, while holding pressure constant, there will be no change of entropy with pressure while holding temperature constant. This occurs with liquid H_2O at about 39.2 F for a pressure of 14.7 lb/in.^{2} abs and indicates that this pressure line should cross the saturated liquid line at this temperature on the T-S diagram.

The right side of both Eqs. (25) and (26) may be evaluated by performing the partial differentiation indicated upon the Equation of State for the desired region. This results in an expression for the left side of these equations which may be used to check the consistency of the properties indicated.

Energy and Entropy Equations.—The heat transferred to or from a medium depends upon the path followed and may be evaluated in terms of any two coordinates. Thus,

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* The differential of the first coefficient with respect to the second variable [on the right side of Eqs. (17) to (20)] is equal to the differential of the second coefficient with respect to the first variable if the expression is a point function.

$$-dQ = -\left(\frac{\delta Q}{\delta T}\right)_V dT - \left(\frac{\delta Q}{\delta V}\right)_T dV \tag{27}$$

but
$$-\left(\frac{\delta Q}{\delta V}\right)_T = T\left(\frac{\delta S}{\delta V}\right)_T = T\left(\frac{\delta P}{\delta T}\right)_V$$

since $T\,dS = -dQ$, and combining with Eq. (25).

Hence, Eq. (27) becomes

$$-dQ = c_V\,dT + T\left(\frac{\delta P}{\delta T}\right)_V dV \tag{A}$$

In like manner,

$$-dQ = c_P\,dT - T\left(\frac{\delta V}{\delta T}\right)_P dP \tag{B}$$

Equations (A) and (B) are not exact differentials since Q depends upon the path followed instead of the state of the substance.

Since,
$$dU = -dQ - dW$$
$$dU = c_V\,dT + \left[T\left(\frac{\delta P}{\delta T}\right)_V - P\right]dV \tag{C}$$

In like manner,

$$dH = c_P\,dT - \left[T\left(\frac{\delta V}{\delta T}\right)_P - V\right]dP \tag{D}$$

This equation indicates that the enthalpy change between any two conditions depends on a temperature and a pressure effect. Values of H for various gases at $P = 0$ and at various temperatures are obtained by adding U and PV values given in Table XIX, Appendix. These values of H are the equivalent of those which might be computed from $\int c_P dT$, if c_P is a function of temperature only.

The effect of pressure includes the term $(\delta V/\delta T)_P$. Differentiating Eq. (6), holding P constant, results in

$$(\delta V/\delta T)_P = R/P - (\delta v/\delta T)_P \tag{28}$$

Combining Eqs. (6), (28), and (D) and integrating with T constant result in

$$(H_P - H_0)_T = \int_0^P \left[T(\delta v/\delta T)_P - v\right]_T dP \tag{29}$$

Values of v can be obtained from such plots as Chart E, Appendix, and values of $(\delta v/\delta T)_P$ are the slopes of the isobaric plots of v and corresponding

T values. The bracketed term may be plotted against P and the integral evaluated graphically.

It has been shown in the development of Eq. (A) that

$$-\left(\frac{\delta Q}{\delta V}\right)_T = T\left(\frac{\delta P}{\delta T}\right)_V$$

Also, in the saturated region,

$$-\left(\frac{\delta Q}{\delta V}\right)_T = \frac{H_{fg}}{V_{fg}}$$

Therefore,
$$H_{fg} = V_{fg}T\left(\frac{\delta P}{\delta T}\right)_V \qquad (E)$$

This is known as *Clapeyron's* equation and is useful in checking H_{fg}, V_{fg}, and the effect of pressure on the temperature of evaporation, freezing, and sublimation.

The Clapeyron equation may be transformed to a reduced basis which results in

$$H_{fg} = V_{fg}T_rP_c\left(\frac{\delta P_r}{\delta T_r}\right)_V \qquad (a)$$

By dividing Eq. (a), which refers to the medium of unknown data, by the same equation using primes as superscripts to indicate the reference medium results in

$$\frac{dT_r}{dT_r'} = \frac{H_{fg}'V_{fg}T_rP_c}{H_{fg}V_{fg}'T_r'P_c'} \qquad (b)$$

at the same reduced pressure.

Eliminating V_{fg}/V_{fg}' by assuming the compressibility factors in the Equation of State, $PV = ZRT$, are equal for the unknown and reference mediums at the same reduced pressure results in

$$\frac{dT_r/T_r^2}{dT_r'/(T_r')^2} = \frac{H_{fg}'T_c}{H_{fg}T_c'} \qquad (c)$$

Integrating this expression between the limits $T_r = T_r$ and $T_r = 1$, assuming that H_{fg}'/H_{fg} is constant at the same reduced pressure, results in

$$\frac{(1/T_r) - 1}{(1/T_r') - 1} = \frac{H_{fg}'T_c}{H_{fg}T_c'} \qquad (d)^*$$

Equation (d) may be used for evaluating vapor pressures and latent heats for various temperatures provided the vapor pressure of the unknown medium is known at one temperature and also that the critical pressure and temperature are known. This is accomplished by evaluating T_r' for H_2O (or any other well known medium) and T_r for the unknown, both at the same reduced pressure. Thus, the left side of Eq. (d) may be evaluated. Also, since the reduced temperatures of various mediums are nearly the same for the same reduced pressures, both the left and right sides of Eq. (d) may be equated to the value determined for the left side for the one vapor pressure known. These two

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* Seclin, Leonard, Correlating Vapor Pressure and Latent Heat Data, *Ind. Eng. Chem.*, **38**, 402 (1946).

equations may be used for evaluating the saturation temperatures and latent heats for various pressures for the unknown medium.

Equations for entropy are obtained from Eqs. (*A*) and (*B*) by dividing by T. Thus,

$$dS = \frac{c_V\,dT}{T} + \left(\frac{\delta P}{\delta T}\right)_V dV \tag{F}$$

and

$$dS = \frac{c_P\,dT}{T} - \left(\frac{\delta V}{\delta T}\right)_P dP \tag{G}$$

Combining Eqs. (28) and (*G*) results in the expression for entropy in terms involving the residual volume. Thus,

$$S_P - \left[\int \frac{c_P\,dT}{T} - \int_0^P \frac{R\,dP}{P}\right] = \int_0^P \left(\frac{\delta v}{\delta T}\right)_P dP \tag{30}$$

Relations between P, V, T, and the Specific Heats.—The entropy of a medium is a function of the state and consequently Eqs. (*F*) and (*G*) are exact differentials. Applying the test for exactness results in

$$\frac{1}{T}\left(\frac{\delta c_V}{\delta V}\right)_T = \left(\frac{\delta^2 P}{\delta T^2}\right)_V \tag{H}$$

and

$$\frac{1}{T}\left(\frac{\delta c_P}{\delta P}\right)_T = -\left(\frac{\delta^2 V}{\delta T^2}\right)_P \tag{I}$$

Equation (*I*) is known as the *Clausius* relation. It is useful for checking the specific-heat data in the superheated region with the Equation of State for the same region.

Eliminating *S* between Eqs. (*F*) and (*G*) results in

$$c_P - c_V = T\left[\left(\frac{\delta V}{\delta T}\right)_P \frac{dP}{dT} + \left(\frac{\delta P}{\delta T}\right)_V \frac{dV}{dT}\right]$$

If either *P* or *V* is held constant, the result will be the same, namely,

$$c_P - c_V = T\left[\left(\frac{\delta V}{\delta T}\right)_P \left(\frac{\delta P}{\delta T}\right)_V\right] \tag{J}$$

The Throttling Relationship.—The Energy Equation for the throttling process is $H_1 = H_2$ or $dH = 0$. Writing *H* as a function of *T* and *P*,

$$dH = \left(\frac{\delta H}{\delta T}\right)_P dT + \left(\frac{\delta H}{\delta P}\right)_T dP$$

Changing $\left(\frac{\delta H}{\delta T}\right)_P$ to c_P and applying the resultant equation to the throttling process result in

$$c_P\,dT = -\left(\frac{\delta H}{\delta P}\right)_T dP$$

or

$$\left(\frac{\delta T}{\delta P}\right)_H = -\frac{1}{c_P}\left(\frac{\delta H}{\delta P}\right)_T \tag{K}$$

The left side of this equation is known as the *Joule-Thomson* coefficient. Evaluation of the right side of this equation by performing the indicated differentiation on the *H* equation [see Eq. (*D*)], results in a relationship that may be used to check the results of throttling experiments or the accuracy of the *H* equation.

Application of Relationships. *Perfect Gases.*—The Equation of State for perfect gases is

$$PV = RT$$

Performing the partial differentiation of *V* with respect to *T* holding *P* constant results in

$$\left(\frac{\delta V}{\delta T}\right)_P = \frac{R}{P} \qquad \text{also} \qquad \left(\frac{\delta^2 V}{\delta T^2}\right)_P = 0$$

From Eq. (*I*)

$$c_P = \int -T\left(\frac{\delta^2 V}{\delta T^2}\right)_P dP$$

Hence c_P is not a function of the pressure for mediums in the perfect-gas state.

From Eq. (*D*), in which *H* is a function of *T* and *P*, it is obvious that c_P may also be a function of these two variables or a constant. It has already been shown that c_P is not a function of *P*. Therefore, it is a function of *T* only or a constant.

Substituting the value

$$\left(\frac{\delta V}{\delta T}\right)_P = \frac{R}{P} = \frac{V}{T}$$

in Eq. (*D*) results in

$$dH = c_P\,dT$$

Thus *H* is a function of *T* only, for a perfect gas, and from Eq. (*K*)

$$\left(\frac{\delta H}{\delta P}\right)_T = 0 = -c_P\left(\frac{\delta T}{\delta P}\right)_H$$

Since c_P cannot be zero, the Joule-Thomson coefficient must be zero, indicating no change in the temperature of a perfect gas undergoing a throttling process. With the exception of hydrogen, actual gases initially at pressures near atmospheric experience a slight temperature drop for the throttling process. The temperature of hydrogen increases slightly for this process.

Superheated Ammonia.—The relationships for mediums near the saturated-vapor condition are usually complex. Equation (4), page 288, is the Equation of State for ammonia vapor.

The relation for enthalpy, Eq. (D), requires the first derivative of V with respect to T, holding P constant, and an expression for c_P, which requires the second derivative, also with P constant, Eq. (I). Thus,

$$\left(\frac{\delta V}{\delta T}\right)_P = \frac{A}{P} + \left(\frac{3B}{T^4} + 11\frac{C + DP}{T^{12}} + 19\frac{EP^5}{T^{20}}\right) + f_1(P)$$

and
$$\left(\frac{\delta^2 V}{\delta T^2}\right)_P = -\left(\frac{12B}{T^5} + 132\frac{C + DP}{T^{13}} + 380\frac{EP^5}{T^{21}}\right)$$

Substituting the last expression in Eq. (I) and solving for c_P,

$$c_P = P\left(\frac{12B}{T^4} + 132\frac{C + \frac{D}{2}P}{T^{12}} + \frac{380}{6}\frac{EP^5}{T^{20}}\right) + f(T) \tag{31}$$

Also,
$$T\left(\frac{\delta V}{\delta T}\right)_P - V = \left(\frac{4B}{T^3} + 12\frac{C + DP}{T^{11}} + 20\frac{EP^5}{T^{19}}\right) + F$$

The last two expressions are the coefficients of the variables in Eq. (D), which is an exact differential. If the function of T is given the form

$$f(T) = \frac{A}{T} + G + IT$$

$$H = A \ln T - P\left(\frac{4B}{T^3} + 12\frac{C + \frac{D}{2}}{T^{11}} + \frac{20}{6}\frac{EP^5}{T^{19}}\right) + FP + GT + \frac{IT^2}{2} + K$$

Consolidating the constants into new values,*

$$H = A \log_{10} T - P\left(\frac{B}{T^3} + \frac{C + DP}{T^{11}} + \frac{EP^5}{T^{19}}\right) + FP + GT + IT^2 + K \tag{32}$$

The equation for S is developed in a similar manner. Thus,

$$S = A \log_{10} T - \frac{P}{T}\left(\frac{B}{T^3} + \frac{C + DP}{T^{11}} + \frac{EP^5}{T^{19}}\right) - F \log_{10} P + GT - \frac{I}{T} + f_2(P) + K \tag{33}$$

Use of Compressibility Factors or Residual Volumes.—The evaluation of

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* See data on p. 288.

H and S for actual mediums may be accomplished by the use of residual volumes, perfect-gas data, and Eqs. (29) and (30).

Example.—Determine the enthalpy of CH_4 at 240 F and 4,000 lb/in.² pr. A plot of v vs. T for 0, 1,000, 2,000, 3,000, and 4,000 lb/in.² pr (Fig. 150) permits the determination of the slope $(\delta v/\delta T)_P$ at 240 F for the various pressures.

The bracketed term in Eq. (29) is evaluated as follows:

P	0	1,000 lb/in.²	2,000 lb/in.²	3,000 lb/in.²	4,000 lb/in.²
$(\delta v/\delta T)_P \times 10^5 \text{ft}^3/(\text{lb} \times {}^\circ\text{R})$	−11.74	−11.07	−9.05	−7.26	−5.48
$T(\delta v/\delta T)_P$	−0.0822	−0.0775	−0.0634	−0.0508	−0.0384
v, ft³/lb	0.0180	0.0142	0.0096	0.0046	−0.0002
$[T(\delta v/\delta T)_P - v]$	−0.1002	−0.0917	−0.0730	−0.0554	−0.0382

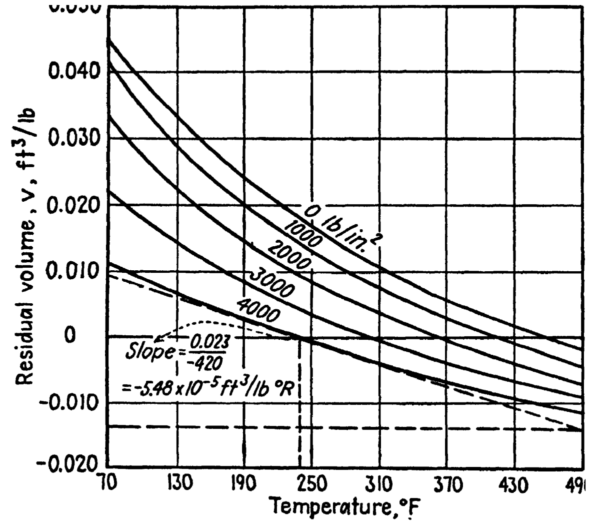

FIG. 150.—Determination of $(\delta v/\delta T)_P$. (This plot is based on data in Chart E, Appendix.)

The plot of the bracketed term vs. P (Fig. 151) is integrated graphically. For an approximate solution the mean height of the curve is estimated to be −0.073 ft³/lb.

Thus, $(H_P - H_0)_{240\text{ F}} = -0.073 \times (4{,}000 - 0) \times 144/778 = -54.1$ Btu/lb.

From Table XIX, Appendix, H at 240 F = 2671 Btu/mole

Then, H at 240 F and 4,000 lb/in.² = 2671 − 16 × 54.1 = 1805 Btu/mole

The value for internal energy may be obtained by subtracting the value for PV from H. In the foregoing case V would be determined from Eq. (6).

In evaluating S from Eq. (30) it is customary to assume that the perfect-gas data are the actual data at a pressure of 1 atm. Thus, the integration is made from this pressure to the pressure of the medium.

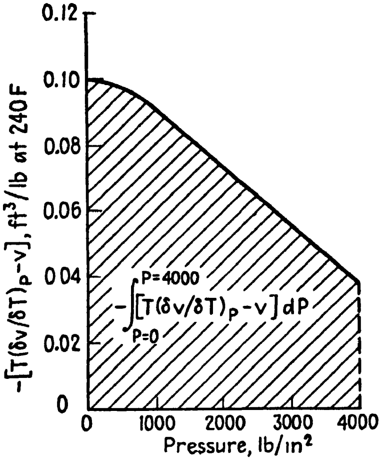

FIG. 151.—Evaluation of H pressure-correction for methane

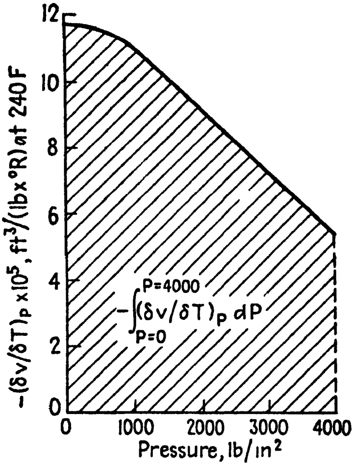

FIG. 152.—Evaluation of S pressure-correction for methane

Example.—Determine the entropy of CH_4 at 240 F and 4,000 lb/in.² pi assuming that the $\int (c_P/T)dT$ values in Table XXII, Appendix, are for a pressure of 14.7 lb/in.² abs.

The $(\delta v/\delta T)_P dP$ may be evaluated graphically from a plot of $(\delta v/\delta T)_P$ vs. P (Fig. 152). For an approximate solution of the right side of Eq. (30), the mean height of the curve is estimated at -9×10^{-5} ft³/(lb × °R). Then,

$$\int_{14.7}^{4,000} (\delta v/\delta T)_P dP = -9 \times 10^{-5} \times (4,000 - 14.7) \times 144/778$$
$$= -0.0664 \text{ Btu/(lb} \times \text{°R)}$$

$$\int_{14.7}^{4,000} R\, dP/P = 1.985 \ln(4,000/14.7) = 11.13 \text{ Btu/(mole} \times \text{°R)}$$

$$S_{4,000} - S_{14.7} = -16 \times 0.0664 - 11.13 = -12.19 \text{ Btu/mole} \times \text{°R)}$$

From Table XXII, Appendix, $S_{1\text{ atm}} = 1.26$ Btu/(mole × °R)

Then, $S_{4,000} = 1.26 - 12.19 = -10.93$ Btu/(mole × °R)

The enthalpy of a mixture of mediums is evaluated from the relation

$$H_P = [(MH)_A + (MH)_B]_{P=0} + \int_0^P (\delta H/\delta P)_T dP \tag{34}$$

in which the bracketed term is the summation of the perfect-gas enthalpies of the constituents A and B at the mixture temperature, and the correction factor refers to the mixture.

From Eq. (29), page 293,

$$\int_0^P \left(\frac{\delta H}{\delta P}\right)_T dP = \int_0^P \left[T\left(\frac{\delta v}{\delta T}\right)_P - v\right] dP \qquad (35)$$

Example.—Determine the enthalpy and internal energy of a mixture of CH_4 and CO_2 having a 0.3583 weight fraction of CH_4 at a pressure of 3,000 lb/in.² and a temperature of 160 F.

Assume 1 mole of CH_4. Then, $(16 \times 0.6417)/(0.3583 \times 44) = 0.651$ moles of CO_2. From Table XIX, Appendix, at 620°R,

$$H_{CO_2} = 1952 \text{ Btu/mole} \qquad H_{CH_4} = 1924 \text{ Btu/mole}$$
$$H_{mix}(\text{ideal}) = 0.651 \times 1952 + 1924 = 3195 \text{ Btu}$$
$$= 1935 \text{ Btu/mole of mixture}$$

At 3,000 lb/in.²

T	100 F	160 F	220 F	280 F
$V = RT/P$	2.000	2.217	2.430	2.643
Z, Table XXIII	0.7103	0.8043	0.8739	0.9226
$(1 - Z)V = v$	0.579	0.434	0.307	0.204

The values of residual volume, $(1 - Z)V$, were plotted against temperature and the slope at 160 F was found to be -2.38×10^{-3} ft³/(lb × °R).

The same procedure was followed for other pressures with the following results

P	200 lb/in.²	1,000 lb/in.²	2,000 lb/in.²	3,000 lb/in.²
$(\delta v/\delta T)_P \times 10^3$	−3.35	−3.33	−3.36	−2.38
$T(\delta v/\delta T)_P$	−2.075	2.065	2.083	1.476
v	0.712	0.681	0.586	0.434
$(\delta H/\delta P)_T$, Eq. (35)	−2.787	−2.746	−2.669	−1.910

Plotting these values against pressure and evaluating the area beneath the curve resulted in a value for ΔH of −1465 Btu/mole of mixture.

$$H \text{ at } 3{,}000 \text{ lb/in.}^2 \text{ and } 160 \text{ F} = 1935 - 1465 = 470 \text{ Btu/mole of mixture}$$

Also,

$$PV = ZRT = 0.8043 \times 1.986 \times 620 = 990 \text{ Btu/mole}$$
$$E = H - PV = 470 - 990 = -520 \text{ Btu/mole}$$

The entropy of a mixture of actual gases is the sum of the entropies of the constituents, assuming perfect-gas relationship, corrected for the effect of pressure on entropy. Usually a pressure of 1 atm for the mixture is close enough to perfect-gas conditions, and the entropy under this condition is determined as indicated in the example on page 106.

The correction for pressure Eq. (G), Appendix, is

$$\Delta S_{\text{corr}} = \int_{1\text{ atm}}^{P} \left(\frac{\delta V}{\delta T}\right)_P dP \tag{36}$$

Hence,

$$S_{\text{mix}} = \Sigma M \int_{T_0}^{T} c_P \frac{dT}{T} - \Sigma MR \ln \frac{M}{M_{\text{mix}}} + \Sigma M S_{0_{T,P}} - \Sigma M \int_{P=1}^{P} \left(\frac{\delta V}{\delta T}\right)_P dP \tag{37}$$

in which M represents the number of moles of each constituent.

The correction factor for pressure may be written in terms of the residual volume. Thus, from Eq. (28) page 293,

$$-\Sigma M \int_{1\text{ atm}}^{P} \left(\frac{\delta V}{\delta T}\right)_P dP = \Sigma M \int_{1\text{ atm}}^{P} \left(\frac{\delta v}{\delta T}\right)_P dP - \Sigma MR \int_{1\text{ atm}}^{P} \frac{dP}{P} \tag{38}$$

Example.—Determine the entropy of a mixture of 1 mole of CH_4 and 0.651 moles of CO_2 at a mixture pressure of 3,000 lb/in.^{2} and a temperature of 160 F.

The entropy of this mixture at 1 atm total pressure is 4.784 Btu/mole × °R). This is the value of the first two terms on the right side of Eq. (37). See the example on page 106.

From the data in the example on page 300, the values of $(\delta v/\delta T)_P$ for the mixture may be plotted against pressure and the area integrated. The mean value for $(\delta v/\delta T)_P$ for the mixture is about -3.28×10^{-3}. Thus,

$$\Sigma M \int_{P=1}^{P} \left(\frac{\delta v}{\delta T}\right)_P dP = -1.651 \times 3.28 \times 10^{-3} \times 2985 \times 144/778 = -2.992 \text{ Btu/°R}$$

$$-\Sigma MR \int_{P=1}^{P} dP/P = -1.651 \times \ln(2985/14.7) = -8.773 \text{ Btu/°R}$$

$$\text{Total pressure correction} = -11.765 \text{ Btu/°R}$$

$$S_{\text{mix}} = 4.784 - 11.765 = -6.981 \text{ Btu/(1.651 moles} \times \text{°R)}$$

EXERCISES

1. Prove the following for perfect gases:

a. c_v is independent of volume.

b. U is a function of the temperature only.

c. $c_P - c_V$ = a constant.

2. Develop the expressions for volume V, and V/v_c in terms of critical and reduced pressure, temperature, and residual volume. *Ans.* $V = RT_cT_r/P_cP_r - v_cv_r$.

3. Develop the expression for $\ln(f/P)$, in which f is the fugacity, in terms of critical and reduced pressure, temperature, and residual volume.

Ans. $\ln(f/P) = -\dfrac{P_cv_c}{RT_cT_r}\displaystyle\int_0^{P_r} v_r dP_r$.

4. Assume that the vapor pressure of ammonia is known only at 0 F (see Table IX). Determine the saturation temperature and latent heat of ammonia at 200 lb/in.^{2} abs based on reduced coordinates and the properties of H_2O.

5. Develop Eqs. (*I*) and (*J*) in terms of critical and reduced values.

Ans. $$\left(\frac{\delta c_P}{\delta P_r}\right)_{T_r} = \frac{P_c v_c T_r}{T_c}\left(\frac{\delta^2 v_r}{\delta T_r^2}\right)_{P_r}. \qquad c_P - c_V = -T\,\frac{\left[\frac{R}{P} - \frac{v_c}{T_c}\left(\frac{\delta v_r}{\delta T_r}\right)_{P_r}\right]^2}{\left[\frac{RT}{P^2} + \frac{v_c}{P_c}\left(\frac{\delta v_r}{\delta P_r}\right)_{T_r}\right]}.$$

6. Derive the National Bureau of Standards equation for S for ammonia vapor.

7. At some assumed temperature compute all the properties of saturated ammonia listed in the ammonia table with the exception of V_f.

8. Determine the enthalpy and entropy of CH_4 at 240 F and 2,000 lb/in.^{2} abs, using data obtained from Figs. 150 to 152.

9. Evaluate and plot the residual volumes for a mixture of CH_4 and CO_2 having a 0.3583 weight fraction of CH_4 at the temperatures listed in Table XXIII, Appendix.

10. Evaluate the enthalpy per mole of mixture at 220 F and 3,000 lb/in.^{2} from the data determined in Exercise 9.

11. Determine the entropy of 1 mole of a mixture of CH_4 and CO_2 having a 0.3583 weight fraction of CH_4 at 220 F and 3,000 lb/in.^{2} from the data evaluated in Exercise 10.

12. Solve the constant-volume cooling process in the example on page 107 considering deviations from perfect-gas behavior.

13. Solve the nonflow adiabatic isentropic process in the example on page 108 considering deviations from perfect-gas behavior.

TABLE I.—RELATION OF ENERGY UNITS

Watt-second (watt-sec)	Foot-pound (ft-lb)	British thermal unit (Btu)	Horsepower-hour (hp-hr)	Kilowatt-hour (kw-hr)
1	0.738			
1.355	1	1.285×10^{-3}		
1.055	778	1	0.393×10^{-3}	
2.684×10^{6}	1.980×10^{6}	2544	1	0.745
3.600×10^{6}	2.656×10^{6}	3413	1.341	1

TABLE II.—SPECIFIC-HEAT EQUATIONS

Gas	Symbol	Equation for c_p in Btu/(mole × °R)	Range, °R	Source
Oxygen.......	O_2	$c_p = 11.515 - \frac{172}{\sqrt{T}} + \frac{1530}{T}$	540–5000	1
Nitrogen.......	N_2	$c_p = 9.47 - \frac{3.47 \times 10^3}{T} + \frac{1.16 \times 10^6}{T^2}$	540–5000	1
Air	....	$c_p = 9.85 - \frac{36.1}{\sqrt{T}} - \frac{2387}{T} + \frac{0.905 \times 10^6}{T^2}$	540–5000	1
Hydrogen	H_2	$c_p = 5.76 + \frac{0.578}{1000} T + \frac{20}{\sqrt{T}}$	540–5000	1
Carbon monoxide....	CO	$c_p = 9.46 - \frac{3.29 \times 10^3}{T} + \frac{1.07 \times 10^6}{T^2}$	540–5000	1
Steam.	H_2O	$c_p = 19.86 - \frac{597}{\sqrt{T}} + \frac{7500}{T}$	540–5000	1
Carbon dioxide	CO_2	$c_p = 16.2 - \frac{6.53 \times 10^3}{T} + \frac{1.41 \times 10^6}{T^2}$	540–6300	1
Carbon.......	C	$c_p = 0.7041 + 3.488 \times 10^{-3} T - 0.556 \times 10^{-6} T^2$	491.6–1440	2
Methane .	CH_4	$c_p = 4.22 + 8.211 \times 10^{-3} T$	491.6–1800	3
Ethylene.	C_2H_4	$c_p = 6.0 + 8.33 \times 10^{-3} T$	720–1440	3
Ethane	C_2H_6	$c_p = 6.6 + 13.33 \times 10^{-3} T$	720–1440	3
Ethyl alcohol	C_2H_6O	$c_p = 4.5 + 21.1 \times 10^{-3} T$	680–1120	3
Methyl alcohol	CH_4O	$c_p = 2.0 + 16.67 \times 10^{-3} T$	680–1100	3
Benzene...	C_6H_6	$c_p = 6.5 + 28.9 \times 10^{-3} T$	520–1120	3
Octane......	C_8H_{18}	$c_p = 14.4 + 53.3 \times 10^{-3} T$	720–1440	3
Dodecane...	$C_{12}H_{26}$	$c_p = 19.6 + 80.0 \times 10^{-3} T$	720–1440	3

Data sources:

1. SWEIGERT, R. L., and M. W. BEARDSLEY, *Ga. School of Technology, State Eng. Exp. Sta. Bull.* 2 (1938).
2. SCHWARZ, CARL, *Arch. Eisenhüttenw.*, **9**, 389 (1936).
3. PARKS, G. S., and H. M. HUFFMAN, *A.C.S., Mon.* 60 (1932).

TABLE III.—STANDARD ATMOSPHERE

N.A.C.A., Tech. Rept., 538 (1935).

Altitude, ft.	Pressure, in. Hg	Temperature, °F	Altitude, ft	Pressure, in. Hg	Temperature, °F
−4,000	34.51	73.3	17,500	15.25	− 3.46
−3,000	33.31	69.7	18,000	14.94	− 5.26
−2,000	32.15	66.1	18,500	14.63	− 7.06
−1,000	31.02	62.6	19,000	14.33	− 8.68
− 500	30.47	60.8	19,500	14.04	−10.48
Sea level	29.92	59.0	20,000	13.75	−12.28
+500	29.38	57.2	21,000	13.18	−15.88
1,000	28.86	55.4	22,000	12.63	−19.48
1,500	28.33	53.6	23,000	12.10	−23.08
2,000	27.82	51.8	24,000	11.59	−26.50
2,500	27.31	50.0	25,000	11.10	−30.10
3,000	26.81	48.38	26,000	10.62	−33.70
3,500	26.32	46.58	27,000	10.16	−37.30
4,000	25.84	44.78	28,000	9.72	−40.90
4,500	25.36	42.98	29,000	9.29	−44.50
5,000	24.89	41.18	30,000	8.88	−47.92
5,500	24.43	39.38	31,000	8.48	−51.52
6,000	23.98	37.48	32,000	8.10	−55.12
6,500	23.53	35.68	33,000	7.73	−58.72
7,000	23.09	33.88	34,000	7.38	−62.32
7,500	22.65	32.08	35,332	6.93	−67.00
8,000	22.22	30.56	36,000	6.71	−67.00
8,500	21.80	28.76	37,000	6.39	−67.00
9,000	21.38	26.96	38,000	6.10	−67.00
9,500	20.98	25.16	39,000	5.81	−67.00
10,000	20.58	23.36	40,000	5.54	−67.00
10,500	20.18	21.56	42,000	5.04	−67.00
11,000	19.79	19.76	44,000	4.58	−67.00
11,500	19.40	17.96	46,000	4.16	−67.00
12,000	19.03	16.16	48,000	3.781	−67.00
12,500	18.65	14.36	50,000	3.436	−67.00
13,000	18.29	12.56	52,000	3.124	−67.00
13,500	17.93	10.94	54,000	2.839	−67.00
14,000	17.57	9.14	56,000	2.581	−67.00
14,500	17.22	7.34	58,000	2.346	−67.00
15,000	16.88	5.54	60,000	2.132	−67.00
15,500	16.54	3.74	62,000	1.938	−67.00
16,000	16.21	1.94	64,000	1.761	−67.00
16,500	15.89	0.14	66,000	1.601	−67.00
17,000	15.56	− 1.66	68,000	1.455	−67.00

TABLE IV.—CRITICAL DATA

Medium	Symbols	Molecular weight	Critical temp, °R	Critical pressure, lb/in.^{2} abs	Critical volume, ft^3/mole	Data source
Hydrocarbons						
Methane	CH_4	16.032	343	673	1.59	1
Ethane	C_2H_6	30.048	549	717	2.20	1
Propane	C_3H_8	44.064	665	617	3.12	1
n-Butane	C_4H_{10}	58.080	766	529	4.01	1
n-Pentane	C_5H_{12}	72.096	846	485	4.98	1
Benzene	C_6H_6	78.048	1010	701	4.11	1
n-Hexane	C_6H_{14}	86.112	915	433	5.88	1
n-Heptane	C_7H_{16}	100.128	972	394	6.84	1
n-Octane	C_8H_{18}	114.144	1024	361	7.85	1
n-Decane	$C_{10}H_{22}$	142.176	1115	311	9.78	2
Dodecane	$C_{12}H_{26}$	170.208	1195	272	12.08	2
Toluene	....	....	1069	611	5.04	2
Alcohols						
Ethyl alcohol	C_2H_6O	46.048	929	927	1.71	2
Methyl alcohol	CH_4O	32.032	924	1156	1.89	2
Miscellaneous						
Ammonia	NH_3	17.040	730	1638	1.16	2
Carbon monoxide	CO	28.000	242	508	1.44	2
Carbon dioxide	CO_2	44.000	547	1071	1.54	3
Helium	He	4.002	9.4	33.8	0.97	3
Hydrogen	H_2	2.016	59.8	188	1.03	3
Nitrogen	N_2	28.016	227	492	0.90	3
Oxygen	O_2	32.000	278	730	1.19	3
Sulphur dioxide	SO_2	64.060	775	1142	1.97	3
Water	H_2O	18.016	1165	3206	0.906	4

Data sources:

1. EDMISTER, W. C., *Ind Eng Chem.*, **30**, 353 (1938).
2. MEISSNER, H. P., and E. N. REDDING, *Ind. Eng. Chem.*, **34**, 522 (1942).
3. *National Bur. Standards Circ.* 279.
4. KEENAN, J. H., and F. G. KEYES, "Thermodynamic Properties of Steam," John Wiley & Sons, Inc. New York, 1936.

Table V.—Liquid H_2O*

P, lb/in², T, °F, V, ft³/lb, U, Btu/lb, H, Btu/lb, S, Btu/(lb × °R).

Abs press, lb/in.² (sat temp)	T	32	100	200	300	400	500	600	650	680	700	705 4	
	P	0 08854	0 9492	11 526	67 013	247 31	680 8	1542 9	2208 2	2708 1	3093 7	3206 2	
Saturated liquid	V	0 016022	0 016132	0 016634	0 017449	0 018639	0 020432	0 023629	0 02680	0 03054	0 03692	0 05030	Saturated liquid
	U	0	67 97	167 95	269 37	374 12	485 23	610 26	684 8	742 0	802 18	872 86	
	H	0	67 97	167 99	269 59	374 97	487 82	617 0	695 7	757 3	823 3	902 7	
	S	0	0 12948	0 29382	0 43694	0 56638	0 68871	0 68871	0 8828	0 9351	0 9905	1 0580	
200 (381 79)	V	0 016011	0 016121	0 016623	0 017438								0 01839
	U	0 02	67 91	167 78	269 17								354 68
	H	0 61	68 51	168 40	269 82								355 36
	S	0 00003	0 12943	0 29361	0 43683								0 5435
600 (486 21)	V	0 015987	0 016100	0 016600	0 017406	0 018595							0 0201
	U	0 02	67 85	167 46	268 63	373 30							469 4
	H	1 80	69 64	169 30	270 56	375 36							471 6
	S	0 00007	0 12921	0 29308	0 43600	0 056542							0 6720
1 000 (544 61)	V	0 015965	0 016075	0 016580	0 017380	0 018552	0 020368						0 0216
	U	0 03	67 69	167 13	268 12	372 38	483 91						538 4
	H	2 99	70 67	170 20	271 34	375 81	487 68						542 4
	S	0 00015	0 12895	0 29262	0 43530	0 56438	0 68730						0 7430
2 000 (635 82)	V	0 015912	0 016033	0 016526	0 017311	0 018444	0 020154	0 023303					0 0257
	U	0 08	67 34	166 38	266 82	370 17	479 98	605 9					662 2
	H	5 97	73 28	172 50	273 23	377 00	487 44	614 5					671 7
	S	0 00022	0 12830	0 29143	0 43352	0 56181	0 68213	0 8088					0 8619
3 000 (695 36)	V	0 015859	0 015985	0 016474	0 017242	0 018339	0 019961	0 022750	0 025477	0 02882			0 0346
	U	0 19	66 97	165 60	265 51	368 12	476 33	597 5	676 8	729 1			783 4
	H	9 00	75 85	174 75	275 08	378 30	487 41	610 1	691 0	745 1			802 5
	S	0 00028	0 12769	0 29026	0 43182	0 55935	0 67929	0 8007	0 8743	0 9231			0 9731
4,000	V	0 015807	0 015940	0 016424	0 017174	0 018239	0 019787	0 022307	0 024492	0 02654	0 02871	0 02951	
	U	0 18	66 66	164 86	264 28	366 18	473 01	590 5	665 2	705 3	742 5	754 3	
	H	11 88	78 46	177 02	277 00	379 68	487 66	607 0	682 3	724 9	763 8	776 1	
	S	0 00029	0 12706	0 28908	0 43017	0 55698	0 67568	0 7938	0 8622	0 9008	0 9347	0 9453	
5,000	V	0 015755	0 015896	0 016374	0 017119	0 018143	0 019627	0 021936	0 023785	0 02536	0 02675	0 02721	
	U	0 17	66 34	164 14	263 11	364 26	469 91	584 6	654 1	680 8	721 6	730 8	
	H	14 75	81 05	179 29	278 95	381 05	488 07	604 9	676 1	714 3	746 4	756 0	
	S	0 00022	0 12641	0 28790	0 42854	0 55464	0 67230	0 7878	0 8527	0 8872	0 9152	0 9234	

Computed from Keenan and Keyes ' Thermodynamic Properties of Steam " Table IV, p 75 John Wiley & Sons Inc , New York 1936

TABLE VI.—SATURATED H_2O, SOLID, LIQUID, AND VAPOR*

Temp, °F	Press lb/in² abs	Volume, ft³/lb			Internal energy Btu/lb			Enthalpy, Btu/lb			Entropy, Btu/(lb × °R)		
		V_f	V_{fg}	V_g	U_f	U_{fg}	U_g	H_f	H_{fg}	H_g	S_f	S_{fg}	S_g
Solid—Vapor													
−40	0.0019	0.01737	133,900	133,900	−177.00	1174.9	1021.6	−177.00	1221.2	1044.2	−0.3654	2.9087	2.5433
−20	0.0062	0.01739	42,200	42,200	−168.16	1172.7	1017.7	−168.16	1221.2	1053.0	−0.3448	2.7764	2.4316
0	0.0185	0.01742	14,770	14,770	−158.93	1170.0	1011.1	−158.93	1220.7	1061.8	−0.3241	2.6546	2.3305
20	0.0505	0.01745	5,658	5,658	−149.31	1167.0	1004.5	−149.31	1219.9	1070.6	−0.3038	2.5425	2.2387
32	0.0885	0.01747	3,306	3,306	−143.35	1164.9	997.9	−143.35	1219.1	1075.8	−0.2916	2.4793	2.1877
Liquid—Vapor													
32	0.08854	0.01602	3,306	3,306	0.00	1021.7	1021.7	0.00	1075.8	1075.8	0.00	2.1877	2.1877
35	0.09995	0.01602	2,947	2,947	3.02	1019.5	1022.6	3.02	1074.1	1077.1	0.0061	2.1709	2.1770
40	0.12170	0.01602	2,444	2,444	7.95	1016.4	1024.3	8.05	1071.3	1079.3	0.0162	2.0393	2.0948
45	0.14752	0.01602	2,036	2,036	13.05	1012.8	1025.9	13.06	1068.4	1081.5	0.0262	2.1167	2.1429
50	0.17811	0.01603	1,703	1,703	18.07	1009.5	1027.6	18.07	1065.6	1083.7	0.0361	2.0903	2.1264
60	0.2563	0.01604	1,206.6	1,206.7	28.06	1002.9	1031.0	28.06	1059.9	1088.0	0.0555	2.0393	2.0948
70	0.3631	0.01606	867.8	867.9	38.04	995.9	1034.0	38.04	1054.3	1092.3	0.0745	1.9902	2.0647
80	0.5069	0.01608	633.1	633.1	48.02	989.2	1037.2	48.02	1048.6	1096.6	0.0932	1.9428	2.0360
90	0.6982	0.01610	468.0	468.0	57.99	982.5	1040.5	57.99	1042.9	1100.9	0.1115	1.8972	2.0087
100	0.9492	0.01613	350.3	350.4	67.97	975.7	1043.7	67.97	1037.2	1105.2	0.1295	1.8531	1.9826
120	1.6924	0.01620	203.25	203.27	87.91	962.1	1050.0	87.92	1025.8	1113.7	0.1645	1.7694	1.9339
140	2.8886	0.01629	122.99	123.01	107.88	948.4	1056.3	107.89	1014.1	1122.0	0.1984	1.6910	1.8894
160	4.741	0.01639	77.27	77.29	127.88	934.5	1062.4	127.89	1002.3	1130.2	0.2311	1.6174	1.8485
180	7.510	0.01651	50.21	50.23	147.90	920.4	1068.3	147.92	990.2	1138.1	0.2630	1.5480	1.8109
200	11.526	0.01663	33.62	33.64	167.95	906.3	1074.2	167.99	977.9	1145.9	0.2938	1.4824	1.7762
212	14.696	0.01672	26.78	26.80	180.02	897.5	1077.5	180.07	970.3	1150.4	0.3120	1.4446	1.7566
220	17.186	0.01677	23.13	23.15	188.08	891.7	1079.8	188.13	965.2	1153.4	0.3239	1.4201	1.7440
240	24.969	0.01692	16.306	16.323	208.26	876.8	1085.1	208.34	952.2	1160.5	0.3531	1.3609	1.7140
260	35.429	0.01709	11.746	11.763	228.53	861.7	1090.2	228.64	938.7	1167.3	0.3817	1.3043	1.6860
280	49.203	0.01726	8.628	8.645	248.90	846.2	1095.1	249.06	924.7	1173.8	0.4096	1.2501	1.6597
300	67.013	0.01745	6.449	6.466	269.37	830.1	1099.5	269.59	910.1	1179.7	0.4369	1.1980	1.6350
320	89.66	0.01765	4.896	4.914	289.99	813.7	1103.7	290.28	894.9	1185.2	0.4637	1.1478	1.6115
340	118.01	0.01787	3.770	3.788	310.74	796.7	1107.4	311.13	879.0	1190.1	0.4900	1.0992	1.5891
360	153.04	0.01811	2.939	2.957	331.67	779.0	1110.7	332.18	862.2	1194.4	0.5158	1.0519	1.5677
380	195.77	0.01836	2.317	2.335	352.78	760.7	1113.5	353.45	844.6	1198.1	0.5413	1.0059	1.5471
400	247.31	0.01864	1.8447	1.8633	374.12	741.6	1115.7	374.97	826.0	1201.0	0.5664	0.9608	1.5272
450	422.6	0.0194	1.0799	1.0993	428.6	690.0	1118.6	430.1	774.5	1204.6	0.6280	0.8513	1.4793
500	680.8	0.0204	0.6545	0.6749	485.2	631.5	1116.7	487.8	713.9	1201.7	0.6887	0.7438	1.4325
600	1,542.9	0.0236	0.2432	0.2668	610.3	479.0	1089.3	617.0	548.5	1165.5	0.8131	0.5176	1.3307
700	3,093.7	0.0369	0.0392	0.0761	802.2	149.6	951.8	823.3	172.1	995.4	0.9905	0.1484	1.1389
705.4	3,206.2	0.0503	0	0.0503	872.9	0	872.9	902.7	0	902.7	1.0580	0	1.0580

* KEENAN, J. H., and F. G. KEYES, "Thermodynamic Properties of Steam," John Wiley & Sons, Inc., New York, 1936. *U* values computed from data in reference.

TABLE VII.—SATURATED H_2O, LIQUID AND VAPOR*

Press, lb/in.² abs	Temp, °F	Volume, ft³/lb			Internal energy, Btu/lb			Enthalpy, Btu/lb			Entropy, Btu/(lb × °R)		
		V_f	V_{fg}	V_g	U_f	U_{fg}	U_g	H_f	H_{fg}	H_g	S_f	S_{fg}	S_g
In. Hg. 1	79.03	0.01608	652.28	652.3	47.05	990.0	1037.0	47.05	1049.2	1096.3	0.0914	1.9473	2.0387
2	101.14	0.01614	339.18	339.2	69.10	974.9	1044.0	69.10	1036.6	1105.7	0.1316	1.8481	1.9797
3	115.06	0.01618	231.58	231.6	82.99	965.5	1048.5	82.99	1028.6	1111.6	0.1560	1.7896	1.9456
3	141.48	0.01630	118.69	118.71	109.36	947.3	1056.7	109.37	1013.2	1122.6	0.2008	1.6855	1.8863
5	162.24	0.01640	73.50	73.52	130.12	933.0	1063.1	130.13	1001.0	1131.1	0.2347	1.6094	1.8441
10	193.21	0.01659	38.40	38.42	161.14	911.1	1072.2	161.17	982.1	1143.3	0.2835	1.5041	1.7876
15	213.03	0.01672	26.27	26.29	181.06	896.7	1077.8	181.11	969.7	1150.8	0.3135	1.4415	1.7549
20	227.96	0.01683	20.07	20.089	196.10	885.8	1081.9	196.16	960.1	1156.3	0.3356	1.3962	1.7319
25	240.07	0.01692	16.286	16.303	208.34	876.8	1085.1	208.42	952.1	1160.6	0.3533	1.3606	1.7139
30	250.33	0.01701	13.729	13.746	218.73	869.1	1087.8	218.82	945.3	1164.1	0.3680	1.3313	1.6993
40	267.25	0.01715	10.482	10.498	235.90	856.1	1092.0	236.03	933.7	1169.7	0.3919	1.2844	1.6763
50	281.01	0.01727	8.498	8.515	249.93	845.4	1095.3	250.09	924.0	1174.1	0.4110	1.2474	1.6585
60	292.71	0.01738	7.158	7.175	261.90	836.0	1097.9	262.09	915.5	1177.6	0.4270	1.2168	1.6438
70	302.92	0.01748	6.189	6.206	272.38	827.8	1100.2	272.61	907.9	1180.6	0.4409	1.1906	1.6315
80	312.03	0.01757	5.465	5.472	281.76	820.3	1102.1	282.02	901.1	1183.1	0.4531	1.1676	1.6207
100	327.81	0.01774	4.415	4.432	298.08	807.1	1105.2	298.40	888.8	1187.2	0.4740	1.1286	1.6026
120	341.25	0.01789	3.712	3.728	312.05	795.6	1107.6	312.44	877.9	1190.4	0.4916	1.0962	1.5878
140	353.02	0.01802	3.202	3.220	324.35	785.2	1109.6	324.82	868.2	1193.0	0.5069	1.0682	1.5751
160	363.53	0.01815	2.816	2.834	335.39	775.8	1111.2	335.93	859.2	1195.1	0.5204	1.0436	1.5640
180	373.06	0.01827	2.514	2.532	345.42	767.1	1112.5	346.03	850.8	1196.9	0.5325	1.0217	1.5542
200	381.79	0.01839	2.270	2.288	354.68	759.0	1113.7	355.36	843.0	1198.4	0.5435	1.0018	1.5453
220	389.86	0.01850	2.069	2.087	363.27	751.3	1114.6	364.02	835.6	1199.6	0.5537	0.9835	1.5372
240	397.37	0.01860	1.900	1.9183	371.29	744.1	1115.4	372.12	828.5	1200.6	0.5631	0.9667	1.5298
260	404.42	0.01870	1.756	1.7748	378.86	737.3	1116.1	379.76	821.8	1201.5	0.5719	0.9510	1.5229
280	411.05	0.01880	1.6323	1.6511	386.01	730.7	1116.7	386.90	815.3	1202.3	0.5801	0.9363	1.5164
300	417.33	0.01890	1.5244	1.5433	392.79	724.3	1117.1	393.84	809.0	1202.8	0.5879	0.9225	1.5104
320	423.29	0.01899	1.4296	1.4485	399.26	718.3	1117.6	400.39	803.0	1203.4	0.5952	0.9094	1.5046
340	428.97	0.01908	1.3435	1.3645	405.46	712.4	1117.9	406.66	797.1	1203.7	0.6022	0.8970	1.4992
360	434.40	0.01917	1.2704	1.2895	411.39	706.8	1118.2	412.67	791.4	1204.1	0.6090	0.8851	1.4941
380	439.60	0.01925	1.2030	1.2222	417.10	701.3	1118.4	418.45	785.8	1204.3	0.6153	0.8738	1.4891
400	444.59	0.0193	1.1420	1.1613	422.6	695.9	1118.5	424.0	780.5	1204.5	0.6214	0.8630	1.4844
500	467.01	0.0197	0.9081	0.9278	447.6	671.0	1118.6	449.4	755.0	1204.4	0.6487	0.8147	1.4634
600	486.21	0.0201	0.7497	0.7698	469.4	648.3	1117.7	471.6	731.6	1203.2	0.6720	0.7734	1.4454
700	503.10	0.0205	0.6349	0.6554	488.8	627.5	1116.3	491.5	709.7	1201.2	0.6925	0.7371	1.4296
800	518.23	0.0209	0.5478	0.5687	506.6	607.8	1114.4	509.7	688.9	1198.6	0.7108	0.7045	1.4153
1,000	544.61	0.0216	0.4240	0.4456	538.4	571.0	1109.4	542.4	649.4	1191.8	0.7430	0.6467	1.3897
1,500	596.23	0.0235	0.2530	0.2765	605.1	486.1	1091.2	611.6	556.3	1167.9	0.8082	0.5269	1.3351
2,000	635.82	0.0257	0.1621	0.1878	662.2	403.4	1065.6	671.7	463.4	1135.1	0.8619	0.4230	1.2849
2,500	668.13	0.0287	0.1021	0.1307	717.3	313.3	1030.6	730.6	360.5	1091.1	0.9126	0.3197	1.2322
3,000	695.36	0.0346	0.0512	0.0858	783.4	189.3	972.9	802.5	217.8	1020.3	0.9731	0.1885	1.615

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* KEENAN, J. H., and F. G. KEYES, "Thermodynamic Properties of Steam," John Wiley & Sons, Inc., New York, 1936.

TABLE VIII.—SUPERHEATED H_2O, VAPOR*

P, lb/in.^{2} T, °F V, ft^3/lb, U, Btu/lb H, Btu/lb S Btu/(lb × °R)

Press, lb/in.^{2} abs (sat temp)	Prop	Temperature, °F											
		200	300	400	500	600	700	800	900	1000	1200	1400	1600
1 (101.74)	V	392.6	452.3	512.0	571.6	631.2	690.8	750.4	809.9	869.5	988.7	1107.8	1227.0
	U	1077.7	1112.1	1146.9	1182.5	1218.9	1255.9	1293.9	1332.8	1372.6	1455.7	1540.7	1630.4
	H	1150.4	1195.8	1241.7	1288.3	1335.7	1383.8	1432.8	1482.7	1533.5	1637.7	1745.7	1857.5
	S	2.0512	2.1153	2.1720	2.2233	2.2702	2.3137	2.3542	2.3923	2.4283	2.4952	2.5566	2.6137
5 (162.24)	V	78.16	90.25	102.26	114.22	126.16	138.10	150.03	161.95	173.87	197.71	221.6	245.4
	U	1076.5	1111.5	1146.6	1182.4	1218.6	1255.8	1293.8	1332.7	1372.6	1455.7	1540.7	1630.4
	H	1148.8	1195.0	1241.2	1288.0	1335.4	1383.6	1432.7	1482.6	1533.4	1637.7	1745.7	1857.4
	S	1.8718	1.9370	1.9942	2.0456	2.0927	2.1361	2.1767	2.2148	2.2509	2.3178	2.3792	2.4363
14.696 (212.00)	V		30.53	34.68	38.78	42.86	49.64	51.00	55.07	59.13	67.25	75.37	83.48
	U		1109.7	1145.7	1181.7	1218.2	1255.5	1293.6	1332.5	1372.3	1455.5	1540.6	1630.3
	H		1192.8	1239.9	1287.1	1334.8	1383.2	1432.3	1482.3	1533.1	1637.5	1745.5	1857.3
	S		1.8160	1.8743	1.9261	1.9734	2.0170	2.0576	2.0958	2.1319	2.1989	2.2603	2.3174
30 (250.33)	V		14.816	16.897	18.933	20.95	22.96	24.96	26.95	28.95	32.93	36.91	40.89
	U		1107.1	1144.1	1180.6	1217.5	1254.9	1293.1	1332.2	1372.0	1454.7	1540.4	1630.0
	H		1189.3	1237.9	1285.7	1333.8	1382.4	1431.7	1481.8	1532.7	1637.2	1745.3	1857.1
	S		1.7336	1.7937	1.8464	1.8940	1.9379	1.9786	2.0169	2.0530	2.1201	2.1815	2.2386
50 (281.01)	V		8.773	10.065	11.309	12.532	13.744	14.950	16.152	17.352	19.747	22.14	24.53
	U		1103.1	1142.0	1179.2	1216.5	1254.2	1292.6	1331.6	1371.5	1454.1	1540.1	1629.8
	H		1184.3	1235.1	1283.9	1332.5	1381.4	1430.9	1481.1	1532.1	1636.8	1745.0	1856.8
	S		1.6721	1.7349	1.7887	1.8368	1.8809	1.9219	1.9602	1.9964	2.0636	2.1251	2.1822
100 (327.81)	V			4.937	5.589	6.218	6.835	7.446	8.052	8.656	9.860	11.060	12.258
	U			1136.2	1175.7	1214.0	1252.3	1291.1	1330.5	1370.7	1453.2	1539.5	1629.3
	H			1227.6	1279.1	1329.1	1378.9	1428.9	1479.5	1530.8	1635.7	1744.2	1856.2
	S			1.6518	1.7085	1.7581	1.8029	1.8443	1.8829	1.9193	1.9867	2.0484	2.1056
200 (381.79)	V			2.361	2.726	3.060	3.380	3.693	4.002	4.309	4.917	5.521	6.123
	U			1123.0	1168.0	1208.8	1248.5	1288.1	1328.1	1368.5	1451.7	1538.2	1628.3
	H			1210.3	1268.9	1322.1	1373.6	1424.8	1476.2	1528.0	1633.7	1742.6	1855.0
	S			1.5594	1.6240	1.6767	1.7232	1.7655	1.8048	1.8415	1.9044	1.9713	2.0287

* KEENAN, J. H., and F. G KEYES, "Thermodynamic Properties of Steam John Wiley & Sons, Inc , 1936 U values computed from data in reference.

TABLE VIII —SUPERHEATED H_2O, VAPOR* (*Continued*)

Press, lb/in² abs (Sat temp)	Prop	Temperature, °F											
		200	300	400	500	600	700	800	900	1000	1200	1400	1600
300 (417 33)	*V*				1 7675	2 005	2 227	2 442	2 652	2 859	3 269	3 674	4 078
	U				1159 4	1203 4	1244 6	1285 0	1325 5	1366 5	1450 2	1537 0	1627 3
	H				1257 6	1314 7	1368 3	1420 6	1472 8	1525 2	1631 7	1741 0	1853 7
	S				1 5701	1 6268	1 6751	1 7184	1 7582	1 7954	1 8638	1 9260	1 9835
400 (444 59)	*V*				1 2851	1 4770	1 6508	1 8161	1 9767	2 134	2 445	2 751	3 055
	U				1150 0	1197 5	1240 5	1281 9	1323 0	1364 4	1448 6	1535 8	1626 3
	H				1245 1	1306 9	1362 7	1416 4	1469 4	1522 4	1629 6	1739 5	1852 5
	S				1 5281	1 5894	1 6398	1 6842	1 7247	1 7623	1 8311	1 8936	1 9485
500 (467 01)	*V*				0 9927	1 1591	1 3044	1 4405	1 5715	1 6996	1 9504	2 197	2 442
	U				1139 4	1191 3	1236 3	1278 8	1320 6	1362 3	1447 1	1534 6	1625 3
	H				1231 3	1298 6	1357 0	1412 1	1466 0	1519 6	1627 6	1737 7	1851 3
	S				1 4919	1 5588	1 6115	1 6571	1 6982	1 7363	1 8056	1 8683	1 9262
1000 (544 61)	*V*					0 5140	0 6084	0 6878	0 7604	0 8294	0 9615	1 0893	1 2146
	U					1153 7	1212 7	1261 9	1307 5	1351 6	1439 3	1528 4	1620 5
	H					1248 8	1325 3	1389 2	1448 2	1505 1	1617 3	1730 0	1845 0
	S					1 4450	1 5141	1 5670	1 6121	1 6525	1 7245	1 7886	1 8474
2000 (635 82)	*V*						0 2489	0 3074	0 3532	0 3935	0 4668	0 5352	0 6011
	U						1147 9	1221 7	1278 5	1328 8	1423 3	1516 0	1610 0
	H						1240 0	1335 5	1409 2	1474 5	1596 1	1714 1	1832 5
	S						1 3783	1 4576	1 5139	1 5603	1 6384	1 7055	1 7660
3000 (695 36)	*V*						0 0984	0 1760	0 2159	0 2476	0 3018	0 3505	0 3966
	U						1006 1	1169 5	1245 1	1304 3	1406 7	1503 4	1599 7
	H						1060 7	1267 2	1365 0	1441 8	1574 3	1698 0	1819 9
	S						1 1966	1 3690	1 4439	1 4984	1 5837	1 6540	1 7163
4000	*V*						0 0287	0 1052	0 1462	0 1743	0 2192	0 2581	0 2943
	U						742 6	1096 9	1206 1	1277 8	1389 8	1490 6	1589 3
	H						763 8	1174 8	1314 4	1406 8	1552 1	1681 7	1807 2
	S						0 9347	1 2757	1 3827	1 4482	1 5417	1 6154	1 6795
5000	*V*						0 0268	0 0593	0 1036	0 1303	0 1696	0 2027	0 2329
	U						721 6	992 2	1160 6	1248 9	1372 5	1477 7	1579 0
	H						746 4	1047 1	1256 5	1369 5	1529 5	1665 3	1794 5
	S						0 9152	1 1622	1 3231	1 4034	1 5066	1 5839	1 6499

[*] KEENAN, J H and F G KEYES, "Thermodynamic Properties of Steam John Wiley & Sons Inc 1936 *U* values computed from data in reference

TABLE IX.—SATURATED NH_3, LIQUID AND VAPOR*

Temp, °F	Press lb/in² abs	Volume, ft³/lb			Internal energy, Btu/lb			Enthalpy, Btu/lb			Entropy, Btu/(lb×°R)		
		V_f	V_{fg}	V_g	U_f	U_{fg}	U_g	H_f	H_{fg}	H_g	S_f	S_{fg}	S_g
−60	5.55	0.0228	44.71	44.73	−21.2	564.8	543.6	−21.2	610.8	589.6	−0.0517	1.5286	1.4769
−55	6.54	0.0229	38.36	38.38	−15.9	561.1	545.2	−15.9	607.5	591.6	−0.0386	1.5017	1.4631
−50	7.67	0.0230	33.06	33.08	−10.6	557.3	546.7	−10.6	604.3	593.7	−0.0256	1.4753	1.4497
−45	8.95	0.0231	28.90	28.92	− 5.3	553.0	547.7	− 5.3	600.9	595.6	−0.0127	1.4495	1.4368
−40	10.41	0.0232	24.84	24.86	0.0	549.7	549.7	0.0	597.6	597.6	0.0000	1.4242	1.4242
−35	12.05	0.0233	21.66	21.68	5.3	545.9	551.2	5.3	594.2	599.5	0.0126	1.3994	1.4120
−30	13.90	0.0235	18.95	18.97	10.6	542.0	552.6	10.7	590.7	601.4	0.0250	1.3751	1.4001
−25	15.98	0.0236	16.64	16.66	15.9	538.0	553.9	16.0	587.2	603.2	0.0374	1.3512	1.3886
−20	18.30	0.0237	14.66	14.68	21.3	534.0	555.3	21.4	583.6	605.0	0.0497	1.3277	1.3774
−15	20.88	0.0238	12.95	12.97	26.6	530.0	556.6	26.7	580.0	606.7	0.0618	1.3046	1.3664
−10	23.74	0.0239	11.48	11.50	32.0	526.0	558.0	32.1	576.4	608.5	0.0738	1.2820	1.3558
− 5	26.92	0.0241	10.21	10.23	37.4	521.7	559.1	37.5	572.6	610.1	0.0857	1.2597	1.3454
0	30.42	0.0242	9.092	9.116	42.8	517.7	560.5	42.9	568.9	611.8	0.0975	1.2377	1.3352
5	34.27	0.0243	8.126	8.150	48.1	513.5	561.6	48.3	565.0	613.3	0.1092	1.2161	1.3253
10	38.51	0.0245	7.279	7.304	53.6	509.2	562.8	53.8	561.1	614.9	0.1208	1.1949	1.3157
15	43.14	0.0246	6.537	6.562	59.0	504.9	563.9	59.2	557.1	616.3	0.1323	1.1739	1.3062
20	48.21	0.0247	5.885	5.910	64.5	500.6	565.1	64.7	553.1	617.8	0.1437	1.1532	1.2969
25	53.73	0.0249	5.309	5.334	69.9	496.2	566.1	70.2	548.9	619.1	0.1551	1.1328	1.2879
30	59.74	0.0250	4.800	4.825	75.4	491.7	567.1	75.7	544.8	620.5	0.1663	1.1127	1.2790
35	66.26	0.0252	4.348	4.373	79.9	487.2	568.1	81.2	540.5	621.7	0.1775	1.0929	1.2704
40	73.32	0.0253	3.946	3.971	86.5	482.6	569.1	86.8	536.2	623.0	0.1885	1.0733	1.2618
45	80.96	0.0255	3.589	3.614	89.9	478.1	569.9	92.3	531.8	624.1	0.1996	1.0539	1.2535
50	89.19	0.0256	3.268	3.294	97.5	473.3	570.8	97.9	527.3	625.2	0.2105	1.0348	1.2453
55	98.06	0.0258	2.982	3.008	103.1	468.7	571.7	103.5	522.8	626.3	0.2214	1.0159	1.2373
60	107.6	0.0260	2.725	2.751	108.7	463.8	572.5	109.2	518.1	627.3	0.2322	0.9972	1.2294
65	117.8	0.0261	2.494	2.520	114.1	459.2	573.3	114.8	513.4	628.2	0.2430	0.9786	1.2216
70	128.8	0.0263	2.286	2.312	119.9	454.1	574.0	120.5	508.6	629.1	0.2537	0.9603	1.2140
75	140.5	0.0265	2.099	2.125	125.5	449.1	574.6	126.2	503.7	629.9	0.2643	0.9422	1.2065
80	153.0	0.0267	1.928	1.955	131.2	444.1	575.3	132.0	498.7	630.7	0.2749	0.9242	1.1991
85	166.4	0.0269	1.775	1.801	137.0	438.9	575.9	137.8	493.6	631.4	0.2854	0.9064	1.1918
90	180.6	0.0271	1.634	1.661	142.6	433.8	576.4	143.5	488.5	632.0	0.2958	0.8888	1.1846
95	195.8	0.0273	1.507	1.534	148.4	428.6	577.0	149.4	483.2	632.6	0.3062	0.8713	1.1775
100	211.9	0.0275	1.391	1.419	154.1	423.2	577.3	155.2	477.8	633.0	0.3166	0.8539	1.1705
105	228.9	0.0277	1.286	1.313	160.0	417.8	577.8	161.1	472.3	633.4	0.3269	0.8366	1.1635
110	247.0	0.0279	1.189	1.217	165.7	412.4	578.1	167.0	466.7	633.7	0.3372	0.8194	1.1566
115	266.2	0.0281	1.100	1.128	171.6	406.7	578.3	173.0	460.9	633.9	0.3474	0.8023	1.1499
120	286.4	0.0284	1.019	1.047	177.5	401.0	578.5	179.0	455.0	634.0	0.3576	0.7851	1.1427
125	307.8	0.0286	0.945	0.973	183.5	359.1	578.6	185.1	448.9	634.0	0.3679	0.7679	1.1358

* *Nat. Bur. Standards*, Circ. 142 (1923). *U* values computed from data in reference.

TABLE X —SATURATED NH_3, LIQUID AND VAPOR*

Press, lb/in.² abs	Temp, °F	Volume, ft³/lb			Internal energy, Btu/lb			Enthalpy, Btu/lb			Entropy, Btu/(lb×°R)		
		V_f	V_{fg}	V_g	U_f	U_{fg}	U_g	H_f	H_{fg}	H_g	S_f	S_{fg}	S_g
5	−63 11	0 0228	49 29	49 31	−24 5	567 2	542 7	−24 5	612 8	588 3	−0 0599	1 5456	1 4857
10	−41 34	0 0232	25 79	25 81	− 1 4	550 7	549 3	− 1 4	598 5	597 1	−0 0034	1 4310	1 4276
15	−27 29	0 0235	17 65	17 67	13 5	539 8	553 3	13 5	588 8	602 4	0 0318	1 3620	1 3938
20	−16 64	0 0238	13 48	13 50	24 9	531 3	556 2	24 9	581 2	606 2	0 0578	1 3122	1 3700
25	− 7 96	0 0240	10 94	10 96	34 2	524 2	558 4	34 2	574 8	609 1	0 0787	1 2728	1 3515
30	− 0 57	0 0242	9 212	9 236	42 2	518 1	560 3	42 3	569 3	611 6	0 0962	1 2402	1 3364
35	5 89	0 0243	7 967	7 991	49 2	512 6	561 8	49 3	564 3	613 6	0 1113	1 2123	1 3236
40	11 66	0 0245	7 022	7 047	55 4	507 8	563 2	55 6	559 8	615 4	0 1246	1 1879	1 3125
45	16 88	0 0246	6 282	6 307	61 1	503 3	564 4	61 3	555 6	616 9	0 1366	1 1661	1 3027
50	21 67	0 0247	5 685	5 710	66 3	499 1	565 4	66 5	551 7	618 2	0 1475	1 1464	1 2939
55	26 09	0 0249	5 193	5 218	71 2	495 1	566 3	71 4	548 0	619 4	0 1575	1 1284	1 2859
60	30 21	0 0250	4 780	4 805	75 6	491 5	567 1	75 9	544 6	620 5	0 1668	1 1119	1 2787
65	34 06	0 0251	4 428	4 453	79 9	488 0	567 9	80 2	541 3	621 5	0 1754	1 0966	1 2720
70	37 70	0 0252	4 126	4 151	83 9	484 7	568 6	84 2	538 2	622 4	0 1835	1 0823	1 2658
75	41 13	0 0253	3 862	3 887	87 6	481 6	569 2	88 0	535 2	623 2	0 1910	1 0689	1 2599
80	44 40	0 0254	3 630	3 655	91 3	478 6	569 9	91 7	532 3	624 0	0 1982	1 0563	1 2545
90	50 47	0 0256	3 240	3 266	98 0	472 9	570 9	98 4	526 9	625 3	0 2115	1 0330	1 2445
100	56 05	0 0258	2 926	2 952	104 2	467 6	571 8	104 7	521 8	626 5	0 2237	1 0119	1 2356
110	61 21	0 0260	2 667	2 693	110 0	462 7	572 7	110 5	517 0	627 5	0 2348	0 9927	1 2275
120	66 02	0 0262	2 450	2 476	115 4	458 0	573 4	116 0	512 4	628 4	0 2452	0 9749	1 2201
130	70 53	0 0263	2 265	2 291	120 5	453 6	574 1	121 1	508 1	629 2	0 2548	0 9584	1 2132
140	74 79	0 0265	2 105	2 132	125 3	449 4	574 7	126 0	503 9	629 9	0 2638	0 9430	1 2068
150	78 81	0 0266	1 917	1 994	128 4	446 7	575 1	130 6	499 9	630 5	0 2724	0 9285	1 2009
160	82 64	0 0268	1 845	1 872	134 2	441 5	575 7	135 0	496 1	631 1	0 2804	0 9148	1 1952
170	86 29	0 0269	1 737	1 764	138 4	437 7	576 1	139 3	492 3	631 6	0 2881	0 9019	1 1900
180	89 78	0 0271	1 640	1 667	142 4	434 1	576 5	143 3	488 7	632 0	0 2954	0 8896	1 1850
190	93 13	0 0272	1 554	1 581	146 2	430 6	576 8	147 2	485 2	632 4	0 3024	0 8778	1 1802
200	96 34	0 0274	1 475	1 502	149 9	427 2	577 1	150 9	481 8	632 7	0 3090	0 8666	1 1756
210	99 43	0 0275	1 403	1 431	153 5	423 9	577 4	154 6	478 4	633 0	0 3154	0 8559	1 1713
220	102 42	0 0276	1 339	1 367	156 9	420 6	577 5	158 0	475 2	633 2	0 3216	0 8455	1 1671
230	105 30	0 0277	1 279	1 307	160 2	417 6	577 8	161 4	472 0	633 4	0 3275	0 8356	1 1631
240	108 09	0 0278	1 225	1 253	163 5	414 4	577 9	164 7	468 9	633 6	0 3332	0 8260	1 1592
250	110 80	0 0280	1 174	1 202	166 7	411 5	578 2	168 0	465 8	633 8	0 3388	0 8167	1 1555
260	113 42	0 0281	1 127	1 155	169 7	408 6	578 3	171 1	462 8	633 9	0 3441	0 8077	1 1518
270	115 97	0 0282	1 084	1 112	172 7	405 6	578 3	174 1	459 8	633 9	0 3494	0 7989	1 1483
280	118 45	0 0283	1 044	1 072	175 6	402 8	578 4	177 1	456 9	634 0	0 3545	0 7904	1 1449
290	120 86	0 0284	1 006	1 034	178 5	400 0	578 5	180 0	454 0	634 0	0 3594	0 7821	1 1415
300	123 21	0 0285	0 971	0 999	181 3	397 2	578 5	182 9	451 1	634 0	0 3642	0 7741	1 1383

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* *Nat. Bur Standards*, Circ. 142 (1923) U values computed from data in reference

TABLE XI.—SUPERHEATED NH_3, VAPOR*

V in ft³/lb, H and U in Btu/lb, and S in Btu/(lb × °R)

Press, lb/in.² abs (sat temp, °F)	Prop	Sat liquid	Sat vapor	Temperature, °F											
				−40	0	40	80	120	160	200	240	280	320	360	400
10 (−41.34°)	V	0.0232	25.81	25.90	28.58	31.20	33.78	36.35	38.90						
	U	−1.4	549.3	549.8	566.0	581.5	597.1	613.0	629.1						
	H	−1.4	597.1	597.8	618.9	639.3	659.7	680.3	701.1						
	S	−0.0034	1.4276	1.4293	1.4773	1.5200	1.5593	1.5960	1.6307						
20 (−16.64°)	V	0.0238	13.50	......	14.09	15.45	16.78	18.08	19.37	20.66					
	U	24.9	556.2	......	563.3	579.8	595.9	612.0	628.3	644.7					
	H	25.0	606.2	......	615.5	637.0	658.0	678.9	700.0	721.2					
	S	0.0578	1.3700	......	1.3907	1.4356	1.4760	1.5133	1.5485	1.5817					
30 (−0.57°)	V	0.0242	9.236	......	9.250	10.20	11.10	11.99	12.87	13.73	14.59				
	U	42.2	560.3	......	560.5	578.0	594.6	610.9	627.3	644.1	661.0				
	H	42.3	611.6	......	611.9	634.6	656.2	677.5	698.8	720.3	742.0				
	S	0.0962	1.3364	......	1.3371	1.3845	1.4261	1.4642	1.4998	1.5334	1.5653				
40 (11.66°)	V	0.0245	7.047	......	......	7.568	8.268	8.945	9.609	10.27	10.92	11.56			
	U	55.4	563.2	......	......	576.1	593.2	609.9	626.6	643.4	660.4	677.8			
	H	55.6	615.4	......	......	632.1	654.4	676.1	697.7	719.4	741.3	763.4			
	S	0.1246	1.3125	......	......	1.3470	1.3900	1.4288	1.4648	1.4987	1.5309	1.5617			
50 (21.67°)	V	0.0247	5.710	......	......	5.988	6.564	7.117	7.655	8.185	8.710	9.230			
	U	66.3	565.4	......	......	574.1	591.9	608.8	625.8	642.7	659.9	677.3			
	H	66.5	618.2	......	......	629.5	652.6	674.7	696.6	718.5	740.5	762.7			
	S	0.1475	1.2939	......	......	1.3169	1.3613	1.4009	1.4374	1.4716	1.5040	1.5350			
60 (30.21°)	V	0.0250	4.805	......	......	4.933	5.428	5.897	6.352	6.798	7.238	7.675			
	U	75.6	567.1	......	......	572.0	590.4	607.8	625.0	642.0	659.3	676.9			
	H	75.9	620.5	......	......	626.8	650.7	673.3	695.5	717.5	739.7	762.1			
	S	0.1668	1.2787	......	......	1.2913	1.3373	1.3778	1.4148	1.4493	1.4819	1.5130			
70 (37.70°)	V	0.0252	4.151	......	......	4.177	4.615	5.025	5.420	5.807	6.187	6.563			
	U	83.9	568.6	......	......	569.8	588.9	606.7	624.1	641.4	658.7	676.4			
	H	84.2	622.4	......	......	623.9	648.7	671.8	694.3	716.6	738.9	761.4			
	S	0.1835	1.2658	......	......	1.2688	1.3166	1.3579	1.3954	1.4302	1.4631	1.4943			

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* *Nat. Bur. Standards, Circ.* 142 (1923). U values computed from data in reference.

TABLE XI.—SUPERHEATED NH_3, VAPOR*—(*Continued*)

Press lb/in² abs (sat temp, °F)	Prop	Sat liquid	Sat vapor	Temperature °F											
				−40	0	40	80	120	160	200	240	280	320	360	400
80 (44 40°)	*V*	0 0254	3 655				4 005	4 371	4 722	5 063	5 398	5 730			
	U	91 3	569 9				587 4	605 7	623 3	640 6	658 2	675 9			
	H	91 7	624 0				646 7	670 4	693 2	715 6	738 1	760 7			
	S	0 1982	1 2545				1 2981	1 3404	1 3784	1 4136	1 4467	1 4781			
90 (50 47°)	*V*	0 0256	3 266				3 529	3 862	4 178	4 484	4 785	5 081			
	U	98 0	570 9				585 9	604 6	622 4	640 0	657 6	675 4			
	H	98 4	625 3				644 7	668 9	692 0	714 7	737 3	760 0			
	S	0 2115	1 2445				1 2814	1 3247	1 3633	1 3988	1 4321	1 4637			
100 (56 05)	*V*	0 0258	2 952				3 149	3 454	3 743	4 021	4 294	4 562			
	U	104 2	571 8				584 3	603 4	621 5	639 3	657 0	675 0			
	H	104 7	626 5				642 6	667 3	690 8	713 7	736 5	759 4			
	S	0 2237	1 2356				1 2661	1 3104	1 3495	1 3854	1 4190	1 4507			
140 (74 79°)	*V*	0 0265	2 132				2 166	2 404	2 622	2 830	3 030	3 227	3 420		
	U	125 3	574 7				577 7	598 8	618 1	636 6	654 8	673 1	691 4		
	H	126 0	629 9				633 8	661 1	686 0	709 9	733 3	756 7	780 0		
	S	0 2638	1 2068				1 2140	1 2628	1 3045	1 3418	1 3763	1 4088	1 4395		
180 (89 78°)	*V*	0 0271	1 667					1 818	1 999	2 167	2 328	2 484	2 637		
	U	142 4	576 5					593 8	614 4	633 7	652 5	671 1	689 8		
	H	143 3	632 0					654 4	681 0	705 9	730 1	753 9	777 7		
	S	0 2954	1 1850					1 2247	1 2691	1 3081	1 3436	1 3768	1 4081		
220 (102 42°)	*V*	0 0276	1 367					1 443	1 601	1 745	1 881	2 012	2 140	2 265	
	U	156 9	577 5					588 5	610 6	630 8	650 2	669 2	688 2	707 3	
	H	158 0	633 2					647 3	675 8	701 9	726 8	751 1	775 3	799 5	
	S	0 3216	1 1671					1 1917	1 2394	1 2801	1 3168	1 3507	1 3825	1 4127	
260 (113 42°)	*V*	0 0281	1 155					1 182	1 326	1 453	1 572	1 686	1 796	1 904	2 009
	U	169 7	578 3					582 6	606 6	627 8	647 7	667 3	686 5	705 8	725 2
	H	171 1	633 9					639 5	670 4	697 7	723 4	748 4	772 9	797 4	821 9
	S	0 3441	1 1518					1 1617	1 2132	1 2560	1 2938	1 3285	1 3608	1 3914	1 4206
300 (123 21°)	*V*	0 0285	0 999						1 123	1 239	1 346	1 447	1 544	1 639	1 732
	U	181 3	578 5						602 3	624 7	645 3	665 1	684 8	704 3	723 9
	H	182 9	634 0						664 7	693 5	720 0	745 5	770 5	795 3	820 1
	S	0 3642	1 1383						1 1894	1 2344	1 2736	1 3090	1 3419	1 3729	1 4024

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* *Nat Bur. Standards, Circ* 142 (1923) *U* values computed from data in reference

TABLE XII.—SATURATED FREON – 12(CCl₂F₂), LIQUID AND VAPOR*

Temp, °F	Press, lb/in.² abs	Volume, ft³/lb			Internal energy, Btu/lb			Enthalpy, Btu/lb			Entropy, Btu/(lb × °R)		
		V_f	V_{fg}	V_g	U_f	U_{fg}	U_g	H_f	H_{fg}	H_g	S_f	S_{fg}	S_g
−150	0.153	0.00957	179.78	179.79	−23.50	77.49	53.99	−23.50	84.07	60.57	−0.0650	0.2115	0.2065
−140	0.255	0.00965	110.91	110.92	−21.29	77.77	56.48	−21.29	83.01	61.72	−0.0580	0.2597	0.2017
−130	0.412	0.00973	70.93	70.94	−19.10	76.57	57.47	−19.10	81.98	62.88	−0.0512	0.2487	0.1975
−120	0.642	0.00981	46.83	46.84	−16.94	75.43	58.47	−16.94	80.98	64.04	−0.0448	0.2385	0.1937
−110	0.971	0.00989	31.83	31.84	−14.78	74.28	59.50	−14.78	80.00	65.22	−0.0385	0.2288	0.1903
−100	1.430	0.00998	22.19	22.20	−12.64	73.18	60.54	−12.64	79.04	66.40	−0.0325	0.2158	0.1873
− 90	2.054	0.01007	15.85	15.86	−10.51	72.07	61.56	−10.51	78.10	67.59	−0.0266	0.2113	0.1847
− 80	2.885	0.01016	11.56	11.57	− 8.41	71.00	62.59	− 8.40	77.17	68.77	−0.0210	0.2033	0.1823
− 70	3.971	0.01026	8.588	8.608	− 6.31	69.93	63.62	− 6.30	76.25	69.95	−0.0155	0.1957	0.1802
− 60	5.365	0.01036	6.496	6.516	− 4.21	69.86	65.65	− 4.20	75.33	71.13	−0.0102	0.1885	0.1783
− 50	7.125	0.01047	4.409	4.420	− 2.12	68.60	66.48	− 2.11	74.42	72.31	−0.0050	0.1817	0.1767
− 40	9.320	0.01060	3.800	3.911	− 0.02	66.76	66.74	0.00	73.50	73.50	0.0000	0.1752	0.1752
− 30	12.02	0.0107	3.223	3.234	2.01	65.48	67.49	2.03	72.67	74.70	0.0047	0.1692	0.1739
− 20	15.28	0.0108	2.463	2.474	4.04	64.82	68.86	4.07	71.80	75.87	0.0074	0.1633	0.1727
− 10	19.20	0.0109	1.992	2.003	6.10	63.83	69.93	6.14	70.91	77.05	0.0140	0.1577	0.1717
− 5	21.44	0.0110	1.798	1.809	7.16	63.30	70.46	7.20	70.43	77.64	0.0153	0.1560	0.1713
0	23.87	0.0110	1.626	1.637	8.20	62.78	70.98	8.25	69.96	78.21	0.0187	0.1522	0.1709
5	26.51	0.0111	1.474	1.485	9.26	62.24	71.50	9.32	69.47	78.79	0.0210	0.1495	0.1705
10	29.35	0.0112	1.340	1.351	10.33	61.69	72.02	10.39	68.97	79.36	0.0233	0.1468	0.1701
15	32.43	0.0112	1.219	1.230	11.42	61.14	72.56	11.49	68.46	79.94	0.0255	0.1443	0.1698
20	35.75	0.0113	1.110	1.121	12.47	60.60	73.07	12.55	67.94	80.49	0.0278	0.1417	0.1695
25	39.34	0.0114	1.013	1.024	13.58	60.03	73.61	13.66	67.40	81.07	0.0301	0.1391	0.1692
30	43.16	0.0115	0.928	0.939	14.67	59.44	74.11	14.76	66.85	81.61	0.0323	0.1366	0.1689
35	47.29	0.0116	0.851	0.863	15.78	58.83	74.61	15.88	66.29	82.16	0.0346	0.1340	0.1686
40	51.68	0.0116	0.780	0.792	16.89	58.24	75.13	17.00	65.71	82.71	0.0368	0.1315	0.1683
45	56.36	0.0117	0.718	0.730	18.02	57.62	75.64	18.14	65.12	83.25	0.0390	0.1291	0.1681
50	61.39	0.0118	0.661	0.673	19.14	56.99	76.13	19.27	64.51	83.78	0.0413	0.1265	0.1678
55	66.74	0.0119	0.610	0.622	20.26	56.37	76.63	20.41	63.89	84.31	0.0439	0.1235	0.1676
60	72.41	0.0119	0.563	0.575	21.41	55.70	77.11	21.57	63.25	84.82	0.0457	0.1217	0.1674
65	78.42	0.0120	0.520	0.532	22.55	55.05	77.60	22.72	62.60	85.32	0.0480	0.1192	0.1672
70	84.82	0.0121	0.481	0.493	23.71	54.37	78.08	23.90	61.92	85.82	0.0501	0.1169	0.1670
75	91.62	0.0122	0.446	0.458	24.87	53.68	78.55	25.08	61.24	86.32	0.0523	0.1145	0.1668
80	98.76	0.0123	0.413	0.425	26.05	52.98	79.03	26.28	60.52	86.80	0.0545	0.1121	0.1666
85	106.3	0.0124	0.383	0.395	27.24	52.26	79.50	27.48	59.85	87.27	0.0566	0.1098	0.1664
90	114.3	0.0125	0.356	0.368	28.49	51.46	79.95	28.70	59.04	87.74	0.0588	0.1074	0.1662
100	131.6	0.0127	0.306	0.319	30.85	50.00	80.85	31.16	57.46	88.62	0.0632	0.1036	0.1658
110	150.7	0.0129	0.264	0.277	33.29	48.41	81.70	33.65	55.78	89.43	0.0675	0.0979	0.1654
120	171.8	0.0132	0.227	0.240	35.74	46.78	82.52	36.16	53.99	90.15	0.0718	0.0931	0.1649
130	194.9	0.0134	0.295	0.208	38.21	45.05	83.26	38.69	52.07	90.76	0.0761	0.0883	0.1644
140	220.2	0.0138	0.166	0.180	40.68	43.22	83.90	41.24	50.00	91.24	0.0802	0.0834	0.1636

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* Data below −40 F from "Thermodynamic Properties of Freon-12," Kinetic Chemicals, Inc., Wilmington, Del., 1942.
Data above −50 F from "Thermodynamic Properties of Freon-12," *A.S.R.E. Circ.* 12 (1931).

TABLE XIII.—SUPERHEATED FREON −12 (CCl_2F_2), VAPOR*

Press, lb/in.² abs (sat temp)	Prop	Temperature, °F										
		−40	0	40	80	120	160	200	240	280	320	360
5 (−62.2)	*V*	7.363	8.088	8.812	9.533	10.25	10.97	11.69	12.41			
	U	66.91	71.57	76.41	81.48	86.75	92.24	97.93	103.85			
	H	73.72	79.05	84.56	90.30	96.24	102.39	108.75	115.33			
	S	0.1859	0.1979	0.2095	0.2205	0.2311	0.2414	0.2513	0.2610			
10 (−37.2)	*V*	......	4.006	4.371	4.740	5.107	5.470	5.831	6.191			
	U	......	71.40	76.26	81.34	86.62	92.12	97.84	103.74			
	H	......	78.81	84.35	90.11	96.07	102.24	108.63	115.20			
	S	......	0.1861	0.1977	0.2087	0.2194	0.2297	0.2396	0.2493			
15 (−20.8)	*V*	......	2.646	2.895	3.143	3.388	3.632	3.877	4.120			
	U	......	71.24	76.14	81.21	86.50	92.02	97.73	103.66			
	H	......	78.59	84.18	89.94	95.91	102.10	108.49	115.10			
	S	......	0.1791	0.1907	0.2018	0.2125	0.2228	0.2328	0.2425			
20 (−8.0)	*V*	......	1.965	2.155	2.343	2.530	2.716	2.901	3.084			
	U	......	71.12	75.99	81.11	86.42	91.92	97.64	103.57			
	H	......	78.39	83.97	89.78	95.78	101.97	108.38	114.98			
	S	......	0.1741	0.1857	0.1969	0.2076	0.2179	0.2279	0.2377			
25 (2.5)	*V*	......	......	1.714	1.867	2.014	2.164	2.318	2.466			
	U	......	......	75.85	80.96	86.29	91.82	97.52	103.47			
	H	......	......	83.78	89.60	95.61	101.83	108.24	114.88			
	S	......	......	0.1818	0.1930	0.2037	0.2141	0.2241	0.2339			
30 (11.3)	*V*	......	......	1.415	1.544	1.672	1.799	1.923	2.048	2.172		
	U	......	......	75.72	80.86	86.18	91.70	97.44	103.38	109.54		
	H	......	......	83.58	89.43	95.46	101.69	108.12	114.75	121.60		
	S	......	......	0.1785	0.1897	0.2005	0.2109	0.2210	0.2307	0.2402		
40 (26.0)	*V*	......	......	1.044	1.144	1.242	1.340	1.435	1.530	1.625		
	U	......	......	75.47	80.62	85.96	91.50	97.26	103.19	109.37		
	H	......	......	83.20	89.09	95.15	101.42	107.88	114.52	121.40		
	S	......	......	0.1732	0.1846	0.1954	0.2058	0.2159	0.2257	0.2353		

Press lb/in² abs (sat temp)	Prop	Temperature °F										
		−40	0	40	80	120	160	200	240	280	320	360
50 (38 0)	*V* *U* *H* *S*			0 821 75 16 82 76 0 1690	0 904 80 35 88 72 0 1804	0 984 85 72 94 83 0 1913	10 64 91 29 101 14 0 2018	1 142 97 05 107 62 0 2120	1 220 103 02 114 31 0 2218	1 296 109 19 121 18 0 2313		
60 (48 6)	*V* *U* *H* *S*				0 743 80 10 88 35 0 1769	0 812 85 49 94 51 0 1879	0 880 91 07 100 84 0 1985	0 946 96 86 107 36 0 2086	1 012 102 82 114 06 0 2185	1 076 109 02 120 97 0 2281	1 140 115 41 128 07 0 2374	
70 (58 0)	*V* *U* *H* *S*				0 628 79 82 87 96 0 1738	0 689 85 23 94 16 0 1849	0 748 90 85 100 54 0 1956	0 806 99 66 107 10 0 2058	0 863 102 65 113 83 0 2157	0 920 108 84 120 76 0 2253	0 975 115 25 127 88 0 2347	
80 (66 3)	*V* *U* *H* *S*				0 540 79 56 87 56 0 1711	0 596 85 02 93 84 0 1823	0 649 90 65 100 26 0 1930	0 701 96 46 106 84 0 2033	0 751 102 46 113 58 0 2132	0 802 108 66 120 54 0 2229	0 851 115 10 127 70 0 2323	
100 (80 8)	*V* *U* *H* *S*					0 465 84 54 93 15 0 1777	0 510 90 19 99 63 0 1887	0 553 96 05 106 29 0 1989	0 595 102 10 113 11 0 2090	0 636 108 33 120 10 0 2187	0 677 114 75 127 28 0 2282	0 718 121 39 134 68 0 2374
120 (93 3)	*V* *U* *H* *S*					0 377 84 01 92 38 0 1737	0 417 89 70 98 96 0 1847	0 454 95 51 105 70 0 1953	0 491 101 70 112 60 0 2054	0 526 107 98 119 66 0 2152	0 560 114 46 126 90 0 2247	0 595 121 10 134 32 0 2340
140 (104 6)	*V* *U* *H* *S*					0 314 83 4 91 60 0 1702	0 350 89 27 98 34 0 1814	0 383 95 22 105 14 0 1920	0 415 101 34 112 09 0 2023	0 477 107 64 119 22 0 2122	0 477 114 14 126 50 0 2217	0 507 120 75 133 89 0 2311
160 (114 5)	*V* *U* *H* *S*					0 264 82 86 90 68 0 1668	0 298 88 75 97 57 0 1783	0 329 94 81 104 55 0 1891	0 358 101 00 111 60 0 1995	0 387 107 32 118 78 0 2095	0 414 113 86 126 12 0 2191	0 442 120 54 133 63 0 2285

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* Data below 15 lb/in² from "Thermodynamic Properties of Freon-12" Kinetic Chemicals, Inc Wilmington, Del, 1932.
Data above 10 lb/in.² from "Thermodynamic Properties of Freon-12" *A S R E Circ* 12 (1931).

TABLE XIV —SATURATED CO_2, SOLID AND VAPOR*

Temp, °F	Press, lb/in² abs	Volume, ft³/lb			Internal energy, Btu/lb			Enthalpy, Btu/lb			Entropy Btu/(lb × °R)		
		V_f	V_{fg}	V_g	U_f	U_{fg}	U_g	H_f	H_{fg}	H_g	S_f	S_{fg}	S_g
−140	3 18	0 0101	24 310	24 320	−121 5	236 4	114 9	−121 5	250 7	129 2	0 685	0 784	1 469
−130	5 39	0 0101	14 730	14 740	−118 8	234 7	115 9	−118 8	249 4	130 6	0 693	0 757	1 450
−120	8 90	0 0102	9 169	9 179	−116 0	232 9	116 9	−116 0	248 0	132 0	0 701	0 741	1 442
−115	11 31	0 0102	7 269	7 279	−114 6	232 1	117 5	−114 6	247 3	132 7	0 706	0 717	1 423
−110	14 22	0 0102	5 838	5 848	−113 2	231 0	117 8	−113 2	246 4	133 2	0 710	0 705	1 414
−108	15 57	0 0103	5 348	5 358	−112 6	230 6	118 0	−112 6	246 0	133 4	0 711	0 700	1 411
−106	17 04	0 0103	4 901	4 911	−112 0	230 1	118 1	−112 0	245 6	133 6	0 713	0 695	1 408
−104	18 63	0 0103	4 495	4 505	−111 3	229 6	118 3	−111 3	245 2	133 9	0 715	0 690	1 405
−102	20 36	0 0103	4 128	4 138	−110 7	229 2	118 5	−110 7	244 8	134 1	0 717	0 684	1 401
−100	22 22	0 0103	3 794	3 804	−110 1	228 8	118 7	−110 1	244 4	134 3	0 719	0 679	1 398
− 98	24 22	0 0103	3 489	3 499	−109 5	228 2	118 7	−109 5	243 9	134 4	0 720	0 675	1 395
− 96	26 39	0 0104	3 212	3 222	−109 0	227 7	118 8	−108 9	243 4	134 5	0 722	0 670	1 392
− 94	28 73	0 0104	2 960	2 970	−108 2	227 2	119 0	−108 1	242 9	134 8	0 724	0 665	1 389
− 92	31 26	0 0104	2 728	2 738	−107 5	226 7	119 2	−107 4	242 4	135 0	0 726	0 659	1 385
− 90	33 98	0 0104	2 515	2 525	−106 8	226 0	119 2	−106 7	241 8	135 1	0 728	0 654	1 382
− 89	35 41	0 0104	2 415	2 425	−106 4	225 6	119 2	−106 3	241 5	135 2	0 729	0 652	1 381
− 88	36 89	0 0104	2 320	2 330	−106 0	225 3	119 3	−105 9	241 1	135 2	0 730	0 649	1 379
− 87	38 43	0 0104	2 230	2 240	−105 6	225 0	119 4	−105 5	240 8	135 3	0 731	0 646	1 377
− 86	40 02	0 0104	2 143	2 153	−105 2	224 6	119 4	−105 1	240 4	135 3	0 732	0 644	1 376
− 85	41 67	0 0104	2 060	2 070	−104 5	224 2	119 4	−104 6	240 1	135 5	0 733	0 641	1 374
− 84	43 38	0 0105	1 985	1 995	−104 3	223 8	119 5	−104 2	239 7	135 5	0 734	0 639	1 373
− 83	45 15	0 0105	1 903	1 913	−103 9	223 4	119 5	−103 8	239 3	135 5	0 736	0 635	1 371
− 82	46 98	0 0105	1 829	1 839	−103 5	223 0	119 5	−103 4	238 9	135 5	0 737	0 633	1 370
− 81	48 88	0 0105	1 758	1 768	−103 1	222 7	119 6	−103 0	238 6	135 6	0 738	0 630	1 368
− 80	50 85	0 0105	1 690	1 700	−102 6	222 3	119 7	−102 5	238 2	135 7	0 740	0 626	1 366
− 79	52 89	0 0105	1 625	1 636	−102 1	221 9	119 8	−102 0	237 7	135 7	0 740	0 625	1 365
− 78	55 00	0 0105	1 564	1 575	−101 6	221 4	119 8	−101 5	237 3	135 8	0 741	0 622	1 363
− 77	57 19	0 0105	1 505	1 516	−101 1	220 9	119 8	−101 1	236 9	135 8	0 742	0 620	1 362
− 76	59 45	0 0105	1 449	1 460	−100 6	220 4	119 8	−100 5	236 4	135 8	0 744	0 616	1 360
− 75	61 79	0 0105	1 396	1 407	−100 2	220 0	119 8	−100 2	236 0	135 8	0 745	0 613	1 358
− 74	64 21	0 0105	1 345	1 356	− 99 9	219 7	119 8	− 99 8	235 6	135 8	0 746	0 611	1 357
− 73	66 72	0 0106	1 295	1 306	− 99 5	219 2	119 8	− 99 3	235 1	135 8	0 747	0 608	1 355
− 72	69 33	0 0106	1 246	1 257	− 99 0	218 8	119 8	− 98 9	234 8	135 9	0 748	0 606	1 354
− 71	72 03	0 0106	1 198	1 209	− 98 6	218 4	119.8	− 98 4	234 3	135 9	0 749	0 601	1 352
− 70	74 82	0 0106	1 151	1 162	− 98 1	217 9	119 8	− 98 0	233 9	135 9	0 751	0 600	1 351
− 69 9	75 10	0 0106	1 146	1 157	− 98 0	217 8	119 8	− 97 9	233 8	135 9	0 751	0 600	1 351

* *A S R E Tables* based on the work of Planck and Kuprianoff

TABLE XV.—SATURATED CO_2, LIQUID AND VAPOR*

Temp, °F	Press, lb/in.² abs	Volume, ft³/lb			Internal energy, Btu/lb			Enthalpy, Btu/lb			Entropy, Btu/(lb × °R)		
		V_f	V_{fg}	V_g	U_f	U_{fg}	U_g	H_f	H_{fg}	H_g	S_f	S_{fg}	S_g
−69.9	75.1	0.0136	1.1434	1.1570	−13.9	133.7	119.8	−13.7	149.6	135.9	0.968	0.383	1.351
−66	82.4	0.0137	1.0452	1.0589	−12.2	132.3	120.1	−11.9	148.1	136.2	0.971	0.376	1.347
−62	90.5	0.0138	0.9548	0.9696	−10.4	130.7	120.3	−10.1	146.6	136.5	0.976	0.368	1.344
−58	99.1	0.0139	0.8736	0.8875	− 8.6	129.0	120.4	− 8.3	145.0	136.7	0.980	0.361	1.341
−54	108.4	0.0140	0.8009	0.8149	− 6.8	127.4	120.6	− 6.5	143.4	136.9	0.985	0.353	1.338
−50	118.2	0.0141	0.7351	0.7492	− 5.0	125.8	120.8	− 4.7	141.9	137.2	0.989	0.346	1.335
−46	128.7	0.0142	0.6757	0.6899	− 3.2	124.2	121.0	− 2.9	140.3	137.4	0.994	0.339	1.333
−42	139.9	0.0143	0.6219	0.6362	− 1.4	122.6	121.2	− 1.0	138.7	137.7	0.998	0.332	1.330
−38	151.8	0.0144	0.5732	0.5876	0.4	121.0	121.4	0.9	136.9	137.8	1.002	0.325	1.327
−34	164.4	0.0145	0.5288	0.5433	2.3	119.2	121.5	2.7	135.4	138.1	1.006	0.318	1.324
−30	177.8	0.0147	0.4882	0.5029	4.0	117.6	121.6	4.5	133.7	138.2	1.011	0.311	1.322
−26	192.0	0.0148	0.4513	0.4661	5.8	116.0	121.8	6.3	132.0	138.3	1.015	0.304	1.319
−22	207.0	0.0149	0.4176	0.4325	7.6	114.3	121.9	8.1	130.3	138.4	1.019	0.298	1.317
−18	223.0	0.0150	0.3942	0.4092	9.4	112.6	122.0	10.1	128.5	138.6	1.023	0.291	1.314
−14	239.6	0.0152	0.3514	0.3666	11.3	110.9	122.2	12.0	126.7	138.7	1.027	0.285	1.312
−10	257.3	0.0153	0.3319	0.3472	13.2	109.1	122.3	13.9	124.8	138.7	1.031	0.278	1.309
− 6	275.9	0.0155	0.3076	0.3231	15.0	107.4	122.4	15.9	122.9	138.8	1.036	0.270	1.306
− 2	295.3	0.0156	0.2853	0.3009	16.8	105.7	122.5	17.9	121.0	138.9	1.040	0.264	1.304
2	315.9	0.0158	0.2745	0.2803	18.8	103.7	122.5	19.8	119.0	138.8	1.044	0.258	1.302
6	337.4	0.0160	0.2454	0.2614	20.8	101.7	122.5	21.8	116.9	138.7	1.048	0.251	1.299
10	360.2	0.0161	0.2276	0.2437	22.9	99.5	122.4	24.0	114.7	138.7	1.054	0.244	1.298
14	383.9	0.0163	0.2111	0.2274	24.9	97.4	122.3	26.1	112.5	138.6	1.058	0.238	1.296
18	408.9	0.0165	0.1956	0.2121	27.0	95.3	122.3	28.3	110.1	138.4	1.062	0.231	1.293
22	434.0	0.0167	0.1812	0.1979	29.2	93.0	122.2	30.5	107.7	138.2	1.067	0.224	1.291
26	462.2	0.0170	0.1670	0.1846	31.4	90.7	122.1	32.9	105.1	138.0	1.072	0.216	1.288
30	490.8	0.0172	0.1550	0.1722	33.8	88.2	122.0	35.4	102.4	137.8	1.077	0.209	1.286
34	502.6	0.0174	0.1429	0.1603	36.2	85.6	121.8	37.9	99.5	137.4	1.082	0.201	1.283
38	551.7	0.0177	0.1319	0.1496	38.6	83.0	121.6	40.4	96.5	136.9	1.087	0.193	1.280
42	584.3	0.0180	0.1213	0.1393	41.0	80.4	121.4	42.9	93.4	136.3	1.091	0.186	1.277
46	618.2	0.0183	0.1114	0.1297	43.4	77.6	121.0	45.6	90.1	135.7	1.096	0.178	1.274
50	653.6	0.0187	0.1018	0.1205	46.1	74.3	120.4	48.4	86.6	135.0	1.101	0.170	1.271
58	728.8	0.0195	0.0839	0.1034	51.2	67.6	118.8	54.0	78.7	132.7	1.110	0.154	1.264
66	810.3	0.0205	0.0685	0.0880	57.4	59.5	116.9	60.2	69.5	129.7	1.123	0.132	1.255
74	898.2	0.0219	0.0508	0.0727	64.0	48.7	112.7	67.3	57.2	124.5	1.136	0.107	1.243
82	993.0	0.0246	0.0319	0.0565	74.7	28.8	103.5	76.4	40.2	116.6	1.153	0.074	1.227
87.8	1066.2	0.0345	0.0000	0.0345	90.2	0.0	90.2	97.0	0.0	97.0	1.189	0.0	1.189

* *A.S.R.E. Tables*, based on the work of Planck and Kuprianoff.

TABLE XVI —SUPERHEATED CO_2 VAPOR*

V in ft³/lb, H and U in Btu/lb, and S in Btu/(lb × °R)

Press, lb/in² abs (sat temp)	Prop	Temperature, °F											
		−75	0	50	100	200	300	400	500	750	1000	1400	1800
10 (−117 6)	V	9 280	11 15	12 38	13 61	16 06	18 51	20 96	23 41	29 51	35 61	45 36	55 11
	U	122 1	133 4	141 1	149 2	166 0	183 8	202 5	222 5	275 8	333 2	431 4	534 7
	H	139 3	154 0	164 0	174 4	195 7	218 0	241 3	265 8	330 4	399 1	515 3	636 7
	S	1 452	1 486	1 507	1 526	1 560	1 592	1 620	1 647	1 707	1 758	1 828	1 887
20 (−102 2)	V	4 586	5 542	6 119	6 778	8 016	9 247	10 47	11 70	14 75	17 80	22 68	27 55
	U	121 6	133 0	140 9	148 9	165 8	183 6	202 5	222 4	275 8	333 2	431 4	534 7
	H	138 6	153 5	163 5	174 0	195 5	217 8	241 2	265 7	330 4	399 1	515 3	636 7
	S	1 421	1 455	1 475	1 494	152 9	1 560	1 589	1 616	1 675	1 727	1 797	1 856
40 (−86 0)	V	2 239	2 738	3 053	3 363	3 993	4 615	5 230	5 845	7 377	8 901	11 34	13 78
	U	120 7	132 2	140 0	148 3	165 5	183 4	202 3	222 2	275 7	333 2	431 4	534 7
	H	137 3	152 5	162 6	173 2	195 1	217 6	241 0	265 5	330 3	399 1	515 3	636 7
	S	1 388	1 423	1 443	1 462	1 497	4 529	1 558	1 585	1 64	1 696	1 766	1 825
60 (−75 7)	V	1 456	1 803	2 016	2 225	2 652	3 070	3 481	3 893	4 917	5 934	7 560	9 183
	U	119 8	131 5	139 3	147 8	165 4	183 1	202 2	222 2	275 7	333 1	431 4	534 7
	H	136 0	151 5	161 7	172 5	194 8	217 2	240 8	265 4	330 3	399 0	515 3	636 7
	S	1 359	1 400	1 422	1 442	1 478	1 510	1 539	1 566	1 626	1 677	1 748	1 807
80 (−67 0)	V		1 335	1 498	1 657	1 982	2 298	2 608	2 918	3 686	4 448	5 670	6 887
	U		130 7	138 6	147 3	165 1	182 9	202 0	222 0	275 6	333 1	431 4	534 7
	H		150 5	160 8	171 8	194 4	216 9	240 6	265 2	330 2	399 0	515 3	636 7
	S		1 383	1 407	1 428	1 465	1 497	1 526	1 553	1 613	1 664	1 735	1 794
100 (−57 5)	V		1 055	1 187	1 316	1 579	1 834	2 083	2 333	2 948	3 559	4 536	5 510
	U		129 9	137 9	146 7	164 8	182 8	201 9	221 8	275 6	333 1	431 4	534 7
	H		149 4	159 9	171 0	194 0	216 7	240 4	265 0	330 2	399 0	515 3	636 7
	S		1 371	1 396	1 417	1 454	1 487	1 516	1 543	1 603	1 654	1 709	1 784
140 (−42 1)	V		0 732	0 832	0 925	1 118	1 305	1 485	1 664	2 105	2 541	3 241	3 935
	U		128 5	136 5	145 5	164 4	182 3	201 5	221 6	275 4	333 1	431 3	534 7
	H		147 4	158 0	169 5	193 4	216 1	240 0	264 7	330 0	399 0	515 3	636 7
	S		1 354	1 380	1 401	1 438	1 471	1 500	1 528	1 588	1 639	1 709	1 768

Press, lb/in.² abs (sat temp)	Prop	Temperature, °F											
		−75	0	50	100	200	300	400	500	750	1000	1400	1800
200 (−23.7)	*V*	.....	0.489	0.565	0.638	0.775	0.908	1.035	1.163	1.472	1.779	2.269	2.757
	U	.....	126.3	134.4	143.7	163.6	181.6	201.1	221.3	275.3	333.1	431.2	534.7
	H	.....	144.4	155.3	167.3	192.3	215.2	239.4	264.3	329.8	398.9	515.2	636.7
	S	.....	1.331	1.360	1.383	1.421	1.454	1.484	1.511	1.571	1.623	1.693	1.752
300 (−1.0)	*V*	.....	.....	0.356	0.410	0.507	0.599	0.687	0.773	0.980	1.186	1.513	1.838
	U	.....	.....	130.9	140.8	162.5	180.8	200.2	220.7	275.0	332.9	431.2	534.7
	H	.....	.....	150.7	163.6	190.6	213.8	238.3	263.6	329.4	398.7	515.2	636.7
	S	.....	.....	1.335	1.360	1.401	1.435	1.465	1.493	1.553	1.605	1.675	1.734
600 (44.2)	*V*	.....	.....	0.145	0.182	0.238	0.290	0.336	0.382	0.488	0.592	0.757	0.921
	U	.....	.....	120.9	132.2	158.8	177.3	198.0	218.9	274.0	332.4	430.8	534.4
	H		.....	137.0	152.4	185.3	209.5	235.3	261.3	328.2	398.1	514.9	636.5
	S			1.281	1.311	1.360	1.399	1.432	1.460	1.521	1.573	1.644	1.703
900 (73.8)	*V*	.....	.....	.....	0.100	0.149	0.187	0.220	0.252	0.324	0.394	0.505	0.614
	U	.....	.....	.....	124.5	155.3	174.1	195.6	217.0	273.2	331.8	430.5	534.2
	H	.....	.....	.....	141.2	180.1	205.2	232.2	259.0	327.2	397.5	514.6	636.4
	S	.....	.....	.....	1.280	1.334	1.376	1.411	1.441	1.503	1.555	1.625	1.684
1200	*V*	.....	.....	.....	.....	0.104	0.136	0.162	0.187	0.242	0.295	0.379	0.461
	U	.....	.....	.....	.....	152.3	170.8	193.2	215.1	272.4	331.3	430.2	539.9
	H	.....	.....	.....	.....	175.4	200.9	229.2	256.7	326.2	396.9	514.4	636.2
	S	.....	.....	.....	.....	1.313	1.358	1.395	1.426	1.489	1.542	1.612	1.671
1600	*V*	.....	.....	.....	.....	.....	.....	0.119	0.139	0.181	0.221	0.284	0.346
	U	.....	.....	.....	.....	.....	.....	189.0	212.7	27[illegible]3	330.7	429.6	539.6
	H	.....	.....	.....	.....	.....	.....	224.3	253.7	324.9	396.2	513.9	636.1
	S	.....	.....	.....	.....		.....	1.379	1.412	1.476	1.529	1.599	1.658
2000	*V*	.....	.....		.....		.....	.....	0.109	0.144	0.177	0.228	0.277
	U	.....	.....	.....	.....		.....	.....	210.3	270.3	330.0	429.2	539.5
	H	.....	.....	.....	.....	.....	.....	.....	250.7	323.6	395.4	513.5	636.0
	S	.....	.....		.....		.....		1.398	1.465	1.518	1.589	1.648
3000	*V*	.....	.....	.....	.....	.....	.....	.....	.....	.....	0.118	0.152	0.186
	U	.....	.....	.....	.....	.....	.....	.....	.....	.....	328.2	428.3	538.5
	H	.....	.....	.....	.....	.....	.....	.....	.....	.....	393.5	512.7	635.5
	S	.....	.....	.....	.....	.....	.....	.....	.....	.....	1.497	1.571	1.630

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* Sweigert, R. L., P. Weber, and R. L. Allen, Thermodynamic Properties of Gases, *Ind. Eng. Chem.*, **38**, 185 (1947). *H* and *S* values adjusted to the datum plane of Table XV and *U* values computed by the author.

TABLE XVII.—SATURATED Hg, LIQUID AND VAPOR*

Press, lb/in.^{2}	Temp, °F	Vol, ft^3/lb	Enthalpy, Btu/lb			Internal energy	Entropy, Btu/(lb × °R)		
		V_g	H_f	H_{fg}	H_g	U_g	S_f	S_{fg}	S_g
0.5	415.2	92.85	14.29	127.87	142.16	133.57	0.0215	0.1462	0.1677
1.0	458.1	48.45	15.89	126.92	142.81	133.84	0.0233	0.1383	0.1616
1.5	485.1	33.14	16.90	126.33	143.23	134.03	0.0244	0.1337	0.1581
2.0	505.2	25.32	17.65	125.89	143.54	134.17	0.0251	0.1305	0.1556
3.0	535.4	17.34	18.78	125.22	144.00	134.37	0.0263	0.1258	0.1521
5.0	576.2	10.77	20.30	124.32	144.62	134.65	0.0278	0.1200	0.1478
10	637.3	5.661	22.58	122.98	145.56	135.08	0.0299	0.1121	0.1420
15	676.5	3.892	24.04	122.12	146.16	135.24	0.0312	0.1075	0.1387
25	730.4	2.429	26.05	120.93	146.98	135.74	0.0330	0.1016	0.1346
30	750.9	2.053	26.81	120.48	147.29	135.89	0.0336	0.0995	0.1331
40	784.8	1.576	28.08	119.73	147.81	136.14	0.0346	0.0962	0.1308
50	812.5	1.284	29.11	119.13	148.24	136.36	0.0355	0.0936	0.1291
60	836.1	1.087	29.99	118.61	148.60	136.53	0.0362	0.0915	0.1277
70	856.6	0.944	30.76	118.15	148.91	136.69	0.0367	0.0898	0.1265
80	874.8	0.835	31.44	117.75	149.19	136.73	0.0373	0.0882	0.1255
90	891.6	0.750	32.06	117.38	149.45	136.96	0.0377	0.0869	0.1246
100	906.9	0.681	32.63	117.05	149.68	137.07	0.0381	0.0857	0.1238
110	921.1	0.624	33.16	116.74	149.90	137.19	0.0385	0.0845	0.1230
120	934.4	0.577	33.66	116.44	150.10	137.29	0.0389	0.0835	0.1224
130	946.7	0.536	34.12	116.17	150.29	137.39	0.0392	0.0826	0.1218
140	958.3	0.501	34.55	115.92	150.47	137.48	0.0395	0.0818	0.1213
150	969.4	0.471	34.97	115.67	150.64	137.57	0.0398	0.0809	0.1207
160	979.9	0.444	35.36	115.44	150.80	137.66	0.0401	0.0802	0.1203
170	989.9	0.420	35.73	115.22	150.95	137.74	0.0403	0.0795	0.1198
180	999.6	0.399	36.09	115.01	151.10	137.81	0.0406	0.0788	0.1194

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* SHELDON, L. A., *Trans.*, *A.S.M.E.*, 46, 272 (1924)

TABLE XVIII.—SATURATED H_2O-NH_3, LIQUID AND VAPOR SOLUTIONS*

x = concentration† H in Btu/lb

Press lb/in² gage (sat temp H_2O °F)		$x=0$ H	Temperature °F																										$x=1$ H		Press lb/in² gage (sat temp, NH_3, °F)
			350		300		280		260		240		220		200		150		100		60		20		0		−20				
			x	H	x	H	x	H	x	H	x	H	x	H	x	H	x	H	x	H	x	H	x	H	x	H	x	H			
260	liq	384	114	300	221	230	267	205	315	179	367	155	418	134	478	114	687	99											176	liq	260
(409.3)	vap	1201	505	994	775	861	843	818	892	786	927	756	952	732	971	710	994	664											634	vap	(117.1)
220	liq	370	085	305	189	234	235	207	283	181	332	155	384	132	440	110	620	81											163	liq	220
(395.5)	vap	1200	420	1079	731	881	813	834	871	796	913	766	943	740	965	716	992	667											634	vap	(106.6)
180	liq	353	037	314	135	242	179	213	245	184	294	157	344	132	399	108	557	67	926	124									149	liq	180
(379.5)	vap	1197	218	1107	623	927	736	869	842	809	895	777	931	748	957	723	990	677	999	635									633	vap	(94.7)
140	liq	333	019	317	115	246	158	217	203	188	250	161	300	134	355	105	499	58	760	64									133	liq	140
(360.9)	vap	1194	124	1143	573	946	700	884	795	834	863	791	913	760	945	732	986	683	998	646									631	vap	(80.6)
100	liq	309			068	254	108	225	150	197	195	168	245	139	295	112	434	51	627	25									113	liq	100
(337.9)	vap	1189			423	1009	584	933	712	870	807	819	877	778	923	747	980	692	996	654									628	vap	(63.5)
60	liq	277			011	267	046	238	085	209	126	151	171	151	220	121	355	51	512	4	733	11							88	liq	60
(307.4)	vap	1181			102	1136	348	1078	541	942	685	872	785	819	873	771	968	703	995	662	999	635							623	vap	(40.9)
20	liq	228									030	201	067	172	108	143	230	66	377	−5	507	−40	753	−27					49	liq	20
(258.7)	vap	1167									290	1040	523	932	692	852	916	729	986	672	997	646	999	622					614	vap	(5.5)
10	liq	208											030	181	068	151	152	75	323	−1	449	−46	626	−62	819	−26			34	liq	10
(239.3)	vap	1160											308	1025	550	911	871	750	978	677	996	648	999	625	999	614			609	vap	(−8.4)
0	liq	180													017	164	115	90	249	10	372	−47	514	−82	609	−87	810	−50	13	liq	0
(212.0)	vap	1150													216	1055	771	793	955	689	993	651	998	628	999	617	999	606	602	vap	(−28.0)
10 in	liq																073	99	196	20	314	−42	451	−88	531	−101	646	−100	−2	liq	10 in.
	vap																[illegible]	853	924	703	986	655	997	650	998	620	999	609	597	vap	(−42.1)
20 in	liq																016	113	122	37	228	−27	357	−88	430	−109	511	−123	−25	liq	20 in
	vap																253	1019	823	745	959	665	994	633	997	622	998	611	588	vap	(−63.9)

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* STICKNEY, A. B., "Properties of Ammonia Solutions," A S R E, 1935.

† At 350 F and 260 lb/in² total pr, 0.114 lb of NH_3 will be contained in 1 lb of saturated liquid mixture while 0.505 lb of NH_3 will be contained in 1 lb of saturated vapor mixture.

TABLE XIX.—INTERNAL ENERGY AND RT VALUES FOR GASES*
(Btu/mole above 520°R)

Temp, °R	O_2	N_2	Air	CO_2	H_2O	H_2	CO	CH_4	OH	NO	Monatomic O H A He, etc	PV $=RT$	Temp, °R
420	−500	−485	−488				−485				−298	834	420
440	−400	−388	−390				−388				−238	874	440
460	−300	−291	−292				−291				−179	914	460
480	−200	−194	−195				−194				−119	953	480
500	−100	−97	−98				−97				−60	994	500
520	0	0	0	0	0	0	0	0	0	0	0	1,033	520
536 6†	83	81	81	115	101	80	81	112	84	85	49	1,066	536 6†
540	100	97	97	139	122	96	97	135	101	103	59	1,072	540
560	200	196	196	280	244	193	196	271	202	207	119	1,112	560
580	301	295	295	424	357	291	295	408	304	312	179	1,152	580
600	402	395	395	570	490	390	396	545	407	418	238	1,192	600
700	920	896	897	1,320	1,110	887	896	1,281	914	943	537	1,390	700
800	1,449	1,399	1,403	2,120	1,734	1,386	1,402	2,076	1,422	1,468	834	1,589	800
900	1,989	1,905	1,915	2,965	2,366	1,886	1,913	2,948	1,930	1,994	1,132	1,787	900
1000	2,539	2,416	2,431	3,852	3,009	2,387	2,430	3,901	2,439	2,522	1,430	1,986	1000
1100	3,101	2,934	2,957	4,778	3,666	2,889	2,954	4,932	2,948	3,053	1,728	2,185	1100
1200	3,675	3,461	3,492	5,736	4,339	3,393	3,485	6,038	3,458	3,596	2,026	2,383	1200
1300	4,262	3,996	4,036	6,721	5,030	3,899	4,026	7,217	3,968	4,154	2,324	2,582	1300
1400	4,861	4,539	4,587	7,731	5,740	4,406	4,580	8,467	4,480	4,730	2,622	2,780	1400
1500	5,472	5,091	5,149	8,764	6,468	4,916	5,145	9,786	4,996	5,321	2,920	2,979	1500
1600	6,092	5,652	5,720	9,819	7,212	5,429	5,720	11,172	5,516	5,922	3,218	3,178	1600
1700	6,718	6,224	6,301	10,896	7,970	5,945	6,305	12,622	6,041	6,532	3,516	3,376	1700
1800	7,349	6,805	6,889	11,993	8,741	6,464	6,899	14,122	6,571	7,150	3,813	3,575	1800
1900	7,985	7,393	7,485	13,105	9,526	6,988	7,501	15,698	7,106	7,773	4,111	3,773	1900
2000	8,629	7,989	8,087	14,230	10,327	7,517	8,109	17,316	7,646	8,399	4,409	3,972	2000
2100	9,279	8,502	8,698	15,368	11,146	8,053	8,722	18,980	8,191	9,029	4,707	4,171	2100
2200	9,934	9,203	9,314	16,518	11,983	8,597	9,339	20,684	8,741	9,663	5,005	4,369	2200
2300	10,592	9,817	9,934	17,680	12,835	9,147	9,961	22,425	9,299	10,302	5,303	4,568	2300
2400	11,252	10,435	10,558	18,852	13,700	9,703	10,588	24,201	9,867	10,946	5,601	4,766	2400
2500	11,916	11,056	11,185	20,033	14,578	10,263	11,220	26,009	10,445	11,595	5,899	4,965	2500

Temp, °R	O_2	N_2	Air	CO_2	H_2O	H_2	CO	CH_4	OH	NO	Monatomic O, H, A, He, etc	PV $=RT$	Temp, °R
2600	12,584	11,682	11,817	21,222	15,469	10,827	11,857	27,846	11,039	12,249	6,197	5,164	2600
2700	13,257	12,313	12,453	22,419	16,372	11,396	12,499	29,709	11,628	12,906	6,495	5,362	2700
2800	13,937	12,949	13,095	23,624	17,288	11,970	13,144	31,596	12,223	13,566	6,792	5,561	2800
2900	14,622	13,590	13,742	24,836	18,217	12,549	13,792	33,506	12,823	14,228	7,090	5,759	2900
3000	15,309	14,236	14,394	26,055	19,160	13,133	14,443	35,438	13,428	14,892	7,388	5,958	3000
3100	16,001	14,888	15,051	27,281	20,117	13,723	15,097	37,391	14,037	15,559	7,686	6,157	3100
3200	16,693	15,543	15,710	28,513	21,086	14,319	15,754	39,365	14,649	16,229	7,984	6,355	3200
3300	17,386	16,199	16,369	29,750	22,066	14,921	16,414	41,360	15,264	16,902	8,282	6,554	3300
3400	18,080	16,855	17,030	30,991	23,057	15,529	17,078	43,375	15,882	17,577	8,580	6,752	3400
3500	18,776	17,512	17,692	32,237	24,057	16,143	17,744	45,410	16,504	18,254	8,878	6,951	3500
3600	19,475	18,171	18,356	33,487	25,067	16,762	18,412	47,463	17,131	18,931	9,176	7,150	3600
3700	20,179	18,833	19,022	34,741	26,085	17,385	19,082	49,531	17,762	19,610	9,474	7,348	3700
3800	20,887	19,496	19,691	35,998	27,110	18,011	19,755	51,613	18,397	20,291	9,771	7,547	3800
3900	21,598	20,162	20,363	37,258	28,141	18,641	20,430	53,708	19,036	20,973	10,069	7,745	3900
4000	22,314	20,830	21,037	38,522	29,178	19,274	21,107	55,815	19,678	21,657	10,367	7,944	4000
4100	23,034	21,500	21,714	39,791	30,221	19,911	21,784	57,933	20,324	22,343	10,665	8,143	4100
4200	23,757	22,172	22,393	41,064	31,270	20,552	22,462	60,062	20,975	23,030	10,963	8,341	4200
4300	24,482	22,845	23,073	42,341	32,326	21,197	23,140	62,202	21,631	23,719	11,261	8,540	4300
4400	25,209	23,519	23,755	43,622	33,389	21,845	23,819	64,354	22,292	24,409	11,558	8,738	4400
4500	25,938	24,194	24,437	44,906	34,459	22,497	24,499	66,516	22,957	25,100	11,856	8,937	4500
4600	26,668	24,869	25,120	46,193	35,535	23,154	25,179	68,687	23,626	25,792	12,154	9,136	4600
4700	27,401	25,546	25,805	47,483	36,616	23,816	25,860	70,866	24,297	26,485	12,452	9,334	4700
4800	28,136	26,224	26,491	48,775	37,701	24,480	26,542	73,052	24,969	27,179	12,750	9,533	4800
4900	28,874	26,905	27,180	50,069	38,791	25,418	27,226	75,245	25,643	27,874	13,048	9,731	4900
5000	29,616	27,589	27,872	51,365	39,885	25,819	27,912	77,444	26,319	28,570	13,346	9,930	5000
5100	30,361	28,275	28,566	52,663	40,983	26,492	28,600	79,649	26,997	29,267	13,644	10,129	5100
5200	31,308	28,961	29,262	53,963	42,084	27,166	29,289	81,859	27,677	29,966	13,942	10,327	5200
5300	31,857	29,648	29,958	55,265	43,187	27,842	29,980	84,074	28,360	30,666	14,240	10,526	5300
5400	32,607	30,337	30,655	56,569	44,293	28,519	30,674	86,293	29,045	31,367	14,537	10,724	5400

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* Based upon data of R. L. Hersey, J. E. Eberhardt, and H. C. Hottel, Thermodynamic Properties of the Working Fluid in Internal Combustion Engines, *S.A.E. Trans.*, **31**, 409 (1936), excepting CH_4 data which are based on data in *Cornell U. Eng. Exp. Sta. Bull.* 30 (1942) by F. O. Ellenwood, N. Kulik, and N. R. Gay. Other data below 520°R are based on constant specific heats.

† 536.6°R, is equivalent to 25°C., the standard temperature for calorimeter tests.

TABLE XX.—INTERNAL ENERGY OF GASEOUS FUELS AND PRODUCTS OF COMBUSTION*

(Btu/mole above 520°R)

Temp, °R	CH_4	C_6H_6	C_7H_{16}	$C_{12}H_{26}$	CH_4O	C_2HO_6	$\frac{C_8H_{18} + 59.5\ \text{air}}{60.5}$	$\frac{8CO_2 + 9H_2O + 47N_2}{64}$	$PV = RT$
520	0	0	0	0	0	0	0	0	1033
536.6	112	328	674	994	146	226	90	88	1066
540	135	397	814	1,201	177	274	109	106	1072
560	271	805	1,648	2 433	365	556	220	213	1112
580	408	1,224	2,504	3 697	551	847	332	320	1152
600	545	1 656	3 381	4 993	748	1,146	443	430	1192
700	1,281	3 986	8,088	11 955	1 833	2 769	1,016	979	1390
800	2,076	6 605	13,326	19 716	3 085	4,603	1,600	1,536	1589
900	2,948	9 513	19,099	28 278	4,503	6 648	2,198	2,102	1787
1000	3 901	12 709	25 403	37 639	6 088	8,904	2,811	2,678	1986
1100	4,932	16 195	32,241	47,800	7,840	11 371	3,441	3,267	2185
1200	6,038	19 970	39,612	58 762	9,758	14,049	4,089	3 869	2383
1300	7 217	24 034	47,516	70 523	11 843	16,938	4,754	4,482	2582
1400	8,467	28 387	55 953	83 085	14,095	20 038	5,437	5,107	2780
1500	9 786	33 029	64 923	96 446	16 514	23 349	6,138	5,743	2979
1600	11 172		74 425	110 607			6,856	6,392	3178
1700	12 622		84,461	125 569			7,592	7,054	3376
1800	14 132		95 030	141,330			8,346	7,726	3575
1900	15,698		106 132	157 892			9,116	8,407	3773
2000	17,316		117,767	175 253			9,900	9,098	3972
2100	18,980							9,798	4171
2200	20 684							10,507	4369
2300	22,425							11,224	4568
2400	24,201							11,946	4766
2500	26 009							12,673	4965

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* Values for CH_4, air, CO_2, H_2O, and N_2 were taken from Table XIX. The other values were computed using equations in Table II. These values were extended beyond the range of the equations so that values would be available for computations.

TABLE XXIII.—COMPRESSIBILITY FACTORS FOR MIXTURES OF CH_4 AND CO_2*

Press, lb/in.² abs	Weight fraction of methane					
	100 F					
	0	0.0852	0.19912	0.3583	0.6685	1.0
0	1.000	1.0000	1.0000	1.0000	1.0000	1.0000
200	0.941	0.9512	0.9606	0.9685	0.9760	0.9795
400	0.875	0.8995	0.9202	0.9372	0.9525	0.9598
600	0.798	0.8437	0.8788	0.9063	0.9296	0.9410
800	0.704	0.7830	0.8360	0.8754	0.9075	0.9235
1000	0.580	0.7160	0.7920	0.8451	0.8869	0.9072
1250	0.315	0.6262	0.7350	0.8084	0.8634	0.8892
1500	0.255	0.5388	0.6830	0.7738	0.8428	0.8739
1750	0.272	0.4715	0.6402	0.7460	0.8259	0.8615
2000	0.299	0.4438	0.6100	0.7243	0.8131	0.8526
2500	0.355	0.4565	0.5890	0.7041	0.8027	0.8471
3000	0.411	0.4958	0.6055	0.7103	0.8081	0.8554
3500	0.465	0.5427	0.6400	0.7335	0.8260	0.8758
4000	0.519	0.5921	0.6820	0.7702	0.8565	0.9054
4500	0.572	0.6433	0.7276	0.8130	0.8937	0.9415
5000	0.624	0.6947	0.7755	0.8584	0.9363	0.9813
6000	0.727	0.7976	0.8752	0.9531	1.0291	1.0681
7000	0.828	0.8982	0.9745	1.0502	1.1240	1.1612
8000	0.926	0.9995	1.0745	1.1469	1.2187	1.2555
9000	1.023	1.1012	1.1752	1.2448	1.3130	1.3508
10,000	1.116	1.2035	1.2785	1.3414	1.4078	1.4470
	160 F					
0	1.000	1.0000	1.0000	1.0000	1.0000	1.0000
200	0.958	0.9657	0.9726	0.9786	0.9840	0.9865
400	0.913	0.9307	0.9453	0.9575	0.9685	0.9736
600	0.865	0.8949	0.9181	0.9367	0.9536	0.9617
800	0.814	0.8585	0.8911	0.9167	0.9395	0.9508
1000	0.759	0.8213	0.8646	0.8977	0.9265	0.9410
1250	0.687	0.7742	0.8324	0.8751	0.9120	0.9303
1500	0.609	0.7284	0.8025	0.8546	0.8994	0.9216
1750	0.531	0.6864	0.7755	0.8374	0.8894	0.9152
2000	0.479	0.6500	0.7542	0.8238	0.8814	0.9109
2500	0.452	0.6090	0.7252	0.8078	0.8733	0.9095
3000	0.479	0.6056	0.7180	0.8043	0.8768	0.9165
3500	0.515	0.6259	0.7294	0.8144	0.8907	0.9316
4000	0.556	0.6548	0.7526	0.8362	0.9120	0.9535
4500	0.600	0.6910	0.7831	0.8642	0.9388	0.9807
5000	0.645	0.7322	0.8200	0.8965	0.9710	1.0119
6000	0.735	0.8182	0.9000	0.9736	1.0455	1.0840
7000	0.824	0.9058	0.9848	1.0550	1.1235	1.1615
8000	0.912	0.9935	1.0701	1.1384	1.2050	1.2425
9000	1.000	1.0818	1.1555	1.2220	1.2882	1.3250
10,000	1.088	1.1683	1.2408	1.3055	1.3727	1.4080
	220 F					
0	1.000	1.0000	1.0000	1.0000	1.0000	1.0000
200	0.970	0.9758	0.9811	0.9854	0.9894	0.9913
400	0.938	0.9514	0.9626	0.9711	0.9791	0.9833
600	0.906	0.9269	0.9445	0.9572	0.9693	0.9760
800	0.872	0.9025	0.9269	0.9441	0.9601	0.9695
1000	0.838	0.8786	0.9100	0.9317	0.9518	0.9639
1250	0.796	0.8495	0.8898	0.9174	0.9427	0.9582
1500	0.756	0.8219	0.8712	0.9049	0.9352	0.9539
1750	0.718	0.7962	0.8542	0.8944	0.9296	0.9510
2000	0.684	0.7741	0.8397	0.8860	0.9258	0.9497
2500	0.631	0.7412	0.8183	0.8755	0.9227	0.9512
3000	0.607	0.7253	0.8098	0.8739	0.9288	0.9587
3500	0.611	0.7249	0.8131	0.8793	0.9402	0.9721
4000	0.630	0.7385	0.8271	0.8937	0.9569	0.9912
4500	0.658	0.7605	0.8[illegible]79	0.9138	0.9792	1.0138
5000	0.693	0.7890	0.8724	0.9391	1.0056	1.0395
6000	0.770	0.8567	0.9353	0.9988	1.0651	1.1000
7000	0.849	0.9298	1.006[illegible]	1.0678	1.1325	1.1650
8000	0.929	1.0055	1.080[illegible]	1.1405	1.2027	1.2355
9000	1.007	1.0822	1.1554	1.2150	1.2754	1.3084
10,000	1.084	1.1595	1.2295	1.2896	1.3498	1.3822

* REAMER, H. H., H. H. OLDS, B. H. SAGE, and W. N. LACEY, Methane—Carbon Dioxide System in the Gaseous Region, *Ind. Eng. Chem.*, **36**, 88 (1944), except for the weight fraction of 1.0. These were obtained from *Ind. Eng. Chem.*, **35**, 922 (1943), in a paper by the same authors.

TABLE XXIII.—COMPRESSIBILITY FACTORS FOR MIXTURES OF CH_4 AND CO_2* (*Continued*)

Press, lb/in.² abs	Weight fraction of methane					
	280 F					
	0	0.0852	0.19912	0.3583	0.6685	1.0
0	1.000	1.0000	1.0000	1.0000	1.0000	1.0000
200	0.979	0.9834	0.9872	0.9901	0.9931	0.9947
400	0.957	0.9668	0.9747	0.9805	0.9866	0.9900
600	0.934	0.9503	0.9625	0.9713	0.9805	0.9859
800	0.912	0.9339	0.9507	0.9627	0.9749	0.9825
1000	0.889	0.9179	0.9397	0.9545	0.9699	0.9798
1250	0.862	0.8987	0.9263	0.9453	0.9649	0.9772
1500	0.835	0.8810	0.9145	0.9379	0.9608	0.9758
1750	0.810	0.8643	0.9040	0.9313	0.9583	0.9754
2000	0.787	0.8487	0.8950	0.9267	0.9572	0.9760
2500	0.750	0.8247	0.8820	0.9217	0.9588	0.9807
3000	0.729	0.8125	0.8763	0.9226	0.9650	0.9894
3500	0.720	0.8100	0.8778	0.9289	0.9759	1.0025
4000	0.724	0.8154	0.8865	0.9404	0.9914	1.0192
4500	0.737	0.8290	0.9020	0.9571	1.0109	1.0391
5000	0.759	0.8483	0.9223	0.9788	1.0337	1.0612
6000	0.818	0.8992	0.9721	1.0306	1.0848	1.1134
7000	0.883	0.9592	1.0310	1.0877	1.1423	1.1708
8000	0.952	1.0243	1.0955	1.1495	1.2030	1.2327
9000	1.023	1.0921	1.1610	1.2148	1.2672	1.2975
10,000	1.091	1.1605	1.2268	1.2817	1.3350	1.3635
	340 F					
0	1.000	1.0000	1.0000	1.0000	1.0000	1.0000
200	0.985	0.9886	0.9914	0.9936	0.9959	0.9972
400	0.970	0.9773	0.9831	0.9874	0.9921	0.9948
600	0.954	0.9661	0.9751	0.9816	0.9886	0.9929
800	0.939	0.9553	0.9674	0.9762	0.9857	0.9916
1000	0.924	0.9446	0.9600	0.9712	0.9832	0.9908
1250	0.905	0.9320	0.9515	0.9658	0.9809	0.9905
1500	0.887	0.9197	0.9439	0.9614	0.9793	0.9911
1750	0.870	0.9087	0.9374	0.9575	0.9790	0.9927
2000	0.854	0.8989	0.9321	0.9554	0.9793	0.9950
2500	0.828	0.8839	0.9252	0.9545	0.9838	1.0020
3000	0.812	0.8749	0.9232	0.9580	0.9919	1.0120
3500	0.804	0.8730	0.9261	0.9656	1.0032	1.0250
4000	0.805	0.8770	0.9338	0.9768	1.0178	1.0406
4500	0.812	0.8870	0.9460	0.9917	1.0355	1.0587
5000	0.825	0.9010	0.9625	1.0104	1.0560	1.0787
6000	0.867	0.9412	1.0042	1.0542	1.1014	1.1253
7000	0.919	0.9910	1.0540	1.1044	1.1525	1.1765
8000	0.977	1.0464	1.1105	1.1597	1.2072	1.2315
9000	1.039	1.1058	1.1692	1.2180	1.2640	1.2898
10,000	1.101	1.1664	1.2285	1.2783	1.3250	1.3490
	400 F					
0	1.000	1.0000	1.0000	1.0000	1.0000	1.0000
200	0.989	0.9922	0.9945	0.9963	0.9980	0.9989
400	0.979	0.9845	0.9892	0.9927	0.9962	0.9982
600	0.968	0.9771	0.9841	0.9894	0.9948	0.9979
800	0.957	0.9698	0.9792	0.9864	0.9937	0.9981
1000	0.946	0.9627	0.9748	0.9838	0.9932	0.9986
1250	0.933	0.9544	0.9696	0.9809	0.9928	1.0000
1500	0.921	0.9469	0.9650	0.9789	0.9934	1.0020
1750	0.910	0.9398	0.9611	0.9778	0.9916	1.0047
2000	0.899	0.9340	0.9581	0.9772	0.9967	1.0079
2500	0.882	0.9249	0.9551	0.9791	1.0031	1.0164
3000	0.871	0.9199	0.9560	0.9842	1.0120	1.0273
3500	0.865	0.9180	0.9606	0.9926	1.0232	1.0404
4000	0.866	0.9220	0.9689	1.0041	1.0370	1.0558
4500	0.871	0.9302	0.9805	1.0183	1.0538	1.0728
5000	0.881	0.9431	0.9952	1.0349	1.0725	1.0916
6000	0.913	0.9770	1.0313	1.0736	1.1148	1.1335
7000	0.956	1.0190	1.0748	1.1194	1.1605	1.1803
8000	1.004	1.0670	1.1242	1.1693	1.2097	1.2307
9000	1.057	1.1195	1.1764	1.2209	1.2618	1.2837
10,000	1.114	1.1734	1.2296	1.2752	1.3160	1.3375

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TABLE XXIV.—CHEMICAL ENERGY, HEAT VALUE, AND LATENT HEAT

(For gaseous fuels)

Fuel	Symbol	Reaction	Latent heat, Btu/mole at 77 F	Heat value, Btu/mole at 77 F (Water formed is condensed)		Chemical energy, Btu/mole for the reaction indicated (use only with Tables XIX, XX, and XXV)
				Q_P (const pr)	Q_V (const vol)	
Oxygen	O	$O \rightarrow 0.5O_2$				105,833
Hydroxide	OH	$OH \rightarrow 0.5H_2 + 0.5O_2$				10,700
Nitric oxide	NO	$NO \rightarrow 0.5N_2 + 0.5O_2$				38,746
Hydrogen	H	$H \rightarrow 0.5H_2$				92,822
	H_2	$H_2 + 0.5O_2 \rightarrow H_2O$		122,963[a]	121,365	103,485
Carbon monoxide	CO	$CO + 0.5O_2 \rightarrow CO_2$		121,721[b]	121,188	121,181
Methane	CH_4	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$		383,022[b]	380,891	345,214
Ethylene	C_2H_4	$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$		607,104[c]	604,973	569,298
Ethane	C_2H_6	$C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O$		671,058[d]	668,394	614,866
Ethyl Alcohol	C_2H_5OH	$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$	18,216[e]	606,204[e]	604,072	550,553
Methyl Alcohol	CH_3OH	$CH_3OH + 1.5O_2 \rightarrow CO_2 + 2H_2O$	16,092[e]	328,614[e]	327,045	291,374
Benzene	C_6H_6	$C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O$	14,495[f]	1,417,041[g]	1,414,377	1,360,843
n-Heptane	$C\,H_{16}$	$C\,H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$	15,750[h]	2,085,751[i]	2,080,421	1,937,660
n-Octane	C_8H_{18}	$C_8H_{18} + 12.5O_2 \rightarrow 8CO_2 + 9H_2O$	17,730[h]	2,368,089[i]	2,362,226	2,201,618
n-Dodecane	$C_{12}H_{26}$	$C_{12}H_{26} + 18.5O_2 \rightarrow 12CO_2 + 13H_2O$	23,000[j]	3,498,659[i]	3,490,664	3,258,667

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[a] *Nat. Bur. Standards, Jour. Research*, 6, 1 (1931).

[b] *Nat. Bur. Standards, Jour. Research*, 6, 37 (1931).

[c] *Nat. Bur. Standards, Jour. Research*, 19, 249 (1937).

[d] *Nat. Bur. Standards, Jour. Research*, 12, 735 (1934).

[e] *Nat. Bur. Standards, Jour. Research*, 13, 189 (1934).

[f] *Nat. Bur. Standards, Jour. Research*, 6, 881 (1931).

[g] *Nat. Bur. Standards, Jour. Research*, 2, 375 (1929).

[h] *Nat. Bur. Standards, Jour. Research*, 13, 21 (1934).

[i] *Nat. Bur. Standards, Jour. Research*, 18, 115 (1937).

[j] *Nat. Bur. Standards, Misc. Pub.*, 97 (1929).

TABLE XXV.—REACTION DATA

($Q_P + H_{\text{left side}} = C_{\text{right side - left side}} + H_{\text{right side}}$. See text, pages 182 to 202)

Reaction no	Reaction	Equilibrium relationship: In terms of x and y, indicating part dissociated	Equilibrium relationship: In terms of partial pressures	ΔS, Btu/(mole × °R) at 520°R and 1 atm	Q_P, Btu/mole at 540°R (gaseous H_2O)	C, Btu/mole (based on Table XXIV)
1	$H_2 \rightleftharpoons 2H$	$K_P = \frac{4x^2}{1 - x^2}P$	$K_1 = \frac{[H]^2}{[H_2]}$	21 16*	186,738*	185,644
2	$O_2 \rightleftharpoons 2O$		$K_2 = \frac{[O]^2}{[O_2]}$	27 04*	212,756*	211,666
3	$N_2 \rightleftharpoons 2N$		$K_3 = \frac{[N]^2}{[N_2]}$			
4	$N_2 + O_2 \rightleftharpoons 2NO$	$K_P = \frac{4x^2}{(1 - x)^2}$	$K_4 = \frac{[NO]^2}{[N_2][O_2]}$	5 94*	77,501*	77,492
5	$H_2 + O_2 \rightleftharpoons 2OH$		$K_5 = \frac{[OH]^2}{[H_2][O_2]}$	7 64*†	21,407	21,401
6	$2CO_2 \rightleftharpoons 2CO + O_2$	$K_P = \frac{x^3P}{(1 - x)^2(2 + x)}$	$K_6 = \frac{[CO]^2[O_2]}{[CO_2]^2}$	41 42†	243,450‡	242,362
7	$2H_2O \rightleftharpoons 2H_2 + O_2$		$K_7 = \frac{[H_2]^2[O_2]}{[H_2O]^2}$	21 00†	208,092‡	206,972
8	$2H_2O \rightleftharpoons 2OH + H_2$		$K_8 = \frac{[OH]^2[H_2]}{[H_2O]^2}$	28 64*†	229,499*	228,373
9	$2H_2O + O_2 \rightleftharpoons 4OH$	$K_P = \frac{64x^4P}{(1 - x)^3(x + 3)}$	$K_9 = \frac{[OH]^4}{[H_2O]^2[O_2]}$	36 28*†	262,104	249,774
10	$CO_2 + H_2 \rightleftharpoons CO + H_2O$	$K_P = \frac{x(1 - y)}{y(1 - x)}$	$K_{10} = \frac{[CO][H_2O]}{[CO_2][H_2]}$	10 21†	17,679	17,695
11	$2H_2O + N_2 \rightleftharpoons 2H_2 + 2NO$	$K_P = \frac{4x^2y^2P}{(1 - y)(1 - x)^2(3 + y)}$	$K_{11} = \frac{[H_2]^2[NO]^2}{[H_2O]^2[N_2]}$	26 94*†	285,496	284,464

* HERSEY, EBERHARDT, and HOTTEL *op cit* (Table XIX).

† EASTMAN, E. D., *Chem. Rev.*, **18**, 257 (1936)

‡ *Nat. Bur. Standards, Jour. Research*, **6**, 1 37 (1931).

TABLE XXVI.—LOGARITHMS OF EQUILIBRIUM CONSTANTS*

$$\log_{10}K_P = \log \frac{[C]^c[D]^d}{[A]^a[B]^b} \text{ for reaction } aA + bB \rightleftharpoons cC + dD \text{ (See Table XXV)}$$

$[A]$ = partial pr of A constituent in equilibrium mixture, atm

Temp. °R	(1) $H_2 \rightleftharpoons 2H$	(2) $O_2 \rightleftharpoons 2O$	(3) $N_2 \rightleftharpoons 2N$	(4) $N_2 + O_2 \rightleftharpoons 2NO$	(5) $H_2 + O_2 \rightleftharpoons 2OH$ (8) − (7)	(6) $2CO_2 \rightleftharpoons 2CO + O_2$	(7) $2H_2O \rightleftharpoons 2H_2 + O_2$	(8) $2H_2O \rightleftharpoons 2OH + H_2$	(9) $2H_2O + O_2 \rightleftharpoons 4OH$ 2(5) + (7)	(10) $H_2 + CO_2 \rightleftharpoons H_2O + CO$ $\frac{(6) - (7)}{2}$	(11) $2H_2O + N_2 \rightleftharpoons 2H_2 + 2NO$ (7) + (4)
3000	-7 89	-8 93	-15 68	-4 30	+0 06	-8 68	-9 72	-9 66	-9 60	0 520	-14 02
3100	-7 44	-8 41	-14 97	-4 13	0 11	-8 12	-9 21	-9 10	-8 99	0 545	-13 34
3200	-7 01	-7 93	-14 28	-3 97	0 14	-7 58	-8 72	-8 58	-8 44	0 570	-12 69
3300	-6 61	-7 48	-13 63	-3 81	0 16	-7 08	-8 26	-8 10	-7 94	0 593	-12 07
3400	-6 23	-7 06	-13 01	-3 66	0 19	-6 60	-7 83	-7 64	-7 45	0 616	-11 49
3500	-5 87	-6 67	-12 43	-3 52	0 21	-6 15	-7 42	-7 21	-7 00	0 638	-10 94
3600	-5 53	-6 30	-11 89	-3 39	0 24	-5 72	-7 04	-6 80	-6 76	0 658	-10 43
3700	-5 21	-5 94	-11 37	-3 27	0 27	-5 32	-6 68	-6 41	-6 14	0 676	- 9 95
3800	-4 91	-5 60	-10 88	-3 15	0 29	-4 95	-6 34	-6 05	-5 76	0 693	- 9 49
3900	-4 62	-5 27	-10 41	-3 03	0 31	-4 59	-6 01	-5 70	-5 39	0 709	- 9 04
4000	-4 34	-4 96	- 9 97	-2 92	0 33	-4 25	-5 70	-5 37	-5 04	0 723	- 8 62
4100	-4 08	-4 66	- 9 55	-2 82	0 37	-3 93	-5 41	-5 04	-4 67	0 736	- 8 23
4200	-3 83	-4 38	- 9 16	-2 72	0 40	-3 63	-5 13	-4 73	-4 33	0.748	- 7 85
4300	-3 60	-4 11	- 8 79	-2 62	0 43	-3 35	-4 87	-4 44	-4 01	0 760	- 7 49
4400	-3 38	-3 86	- 8 44	-2 53	0 45	-3 08	-4 62	-4 17	-3 72	0 770	- 7 15
4500	-3 17	-3 62	- 8 10	-2 44	0 48	-2 83	-4 39	-3 91	-3 43	0 779	- 6 83
4600	-2 97	-3 39	- 7 77	-2 36	0 50	-2 59	-4 17	-3 67	-3 17	0 787	- 6 53
4700	-2 77	-3 17	- 7 45	-2 28	0 52	-2 36	-3 95	-3 43	-2 91	0 795	- 6 23
4800	-2 58	-2 96	- 7 15	-2 20	0 53	-2 12	-3 73	-3 20	-2 67	0 803	- 5 93
4900	-2 40	-2 76	- 6 86	-2 13	0 55	-1 90	-3 52	-2 97	-2 41	0 810	- 5 65
5000	-2 22	-2 56	- 6 68	-2 06	0 57	-1 70	-3 33	-2 76	-2 19	0 816	- 5 39
5100	-2 05	-2 37	- 6 31	-2 00	0 59	-1 51	-3 15	-2 56	-1 97	0 823	- 5 15
5200	-1 88	-2 19	- 6 05	-1 94	0 61	-1 32	-2 98	-2 37	-1 76	0 829	- 4 92
5300	-1 72	-2 02	- 5 80	-1 88	0 62	-1 13	-2 80	-2 18	-1 56	0.835	- 4 68
5400	-1 58	-1 86	- 5 56	-1 82	0 62	-0 94	-2 62	-2 00	-1 38	0 840	- 4 44

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* LEWIS, B., and G. VON ELBE, Heat Capacities and Dissociation Equilibria of Gases, *A.C.S. Jour*, **57**, 612 (1935).

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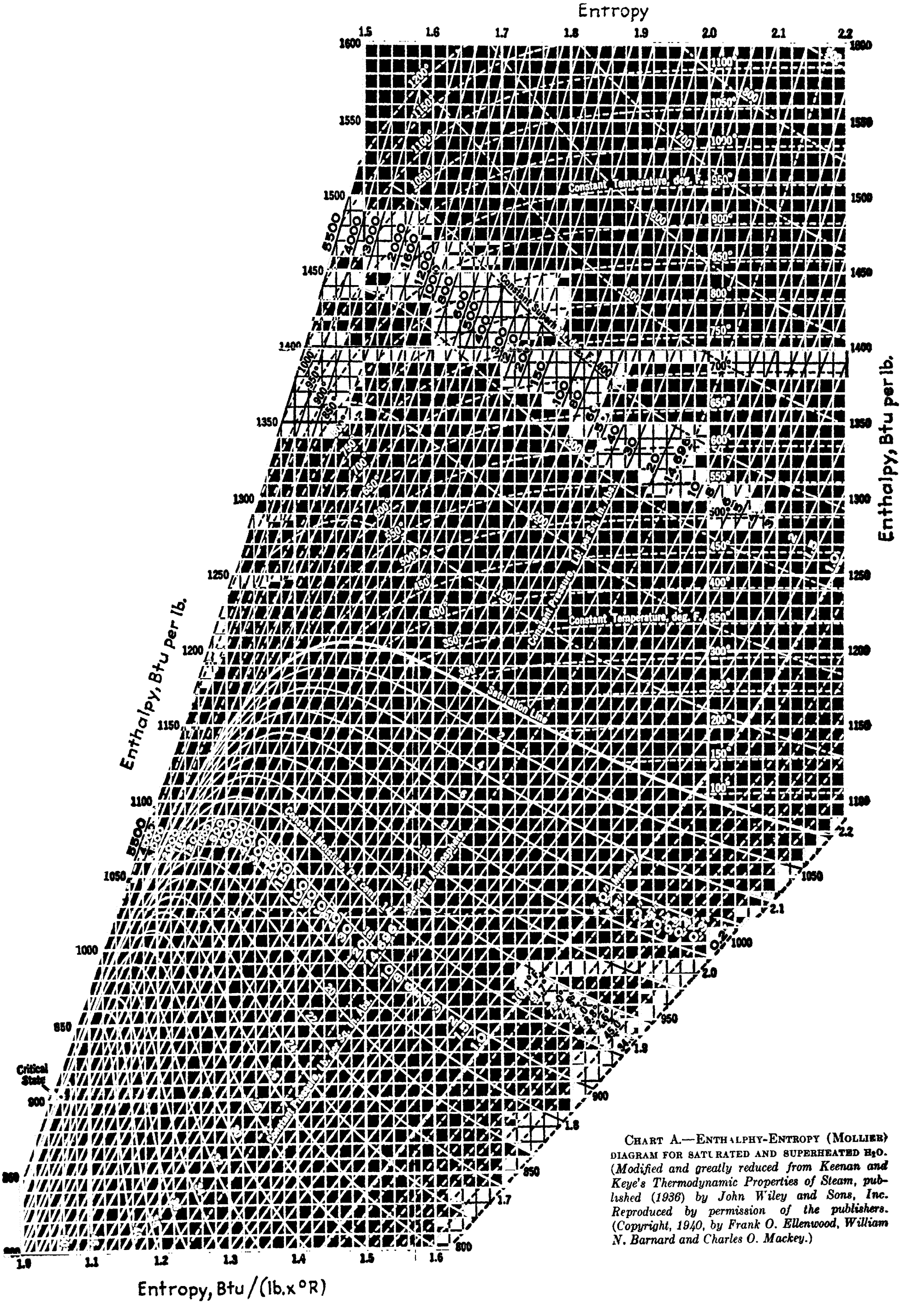


CHART A.—ENTHALPHY-ENTROPY (MOLLIER) DIAGRAM FOR SATURATED AND SUPERHEATED H_2O. (*Modified and greatly reduced from Keenan and Keye's Thermodynamic Properties of Steam, published (1936) by John Wiley and Sons, Inc. Reproduced by permission of the publishers. (Copyright, 1940, by Frank O. Ellenwood, William N. Barnard and Charles O. Mackey.*)

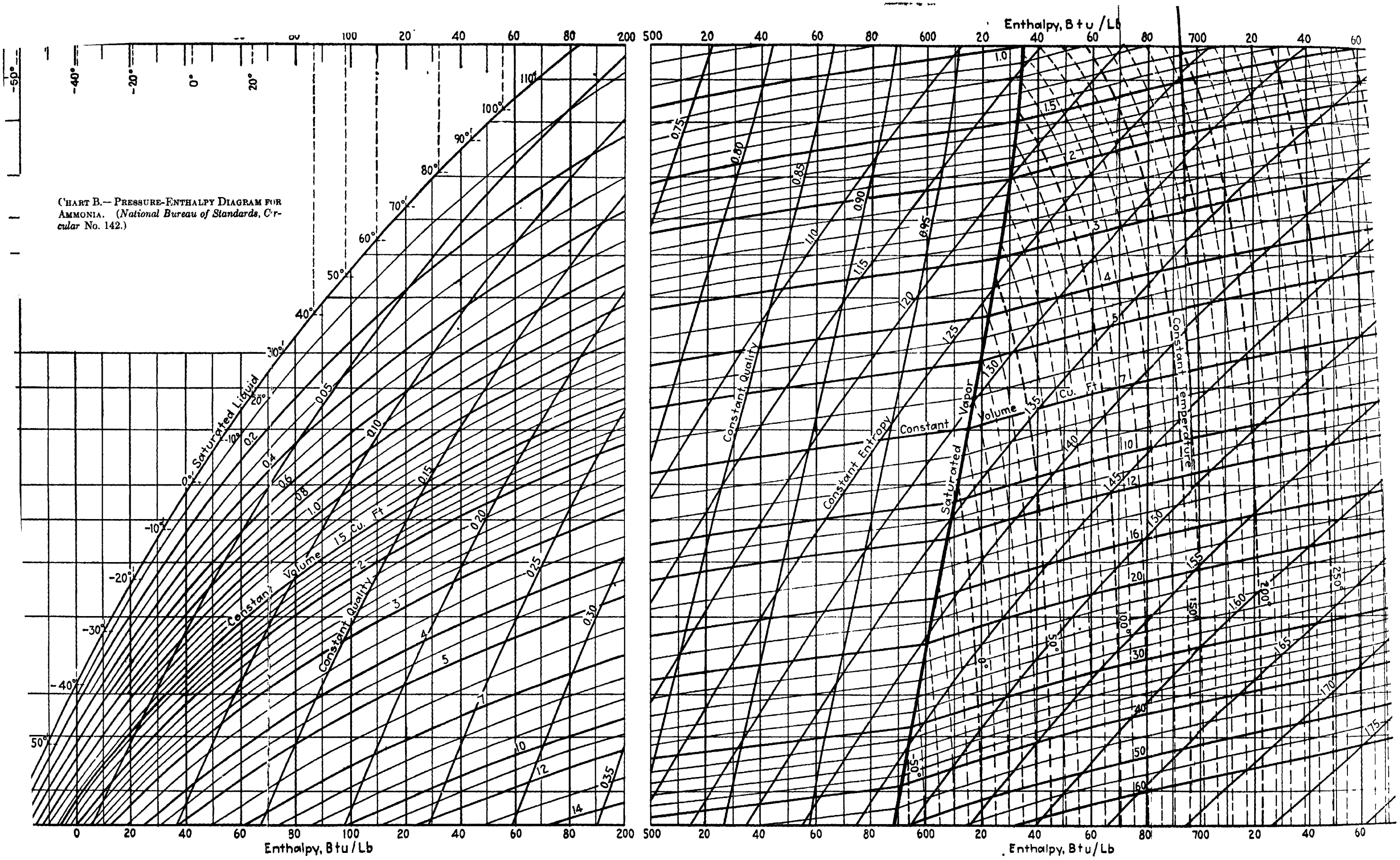


CHART B.—PRESSURE-ENTHALPY DIAGRAM FOR AMMONIA. (*National Bureau of Standards, Circular* No. 142.)

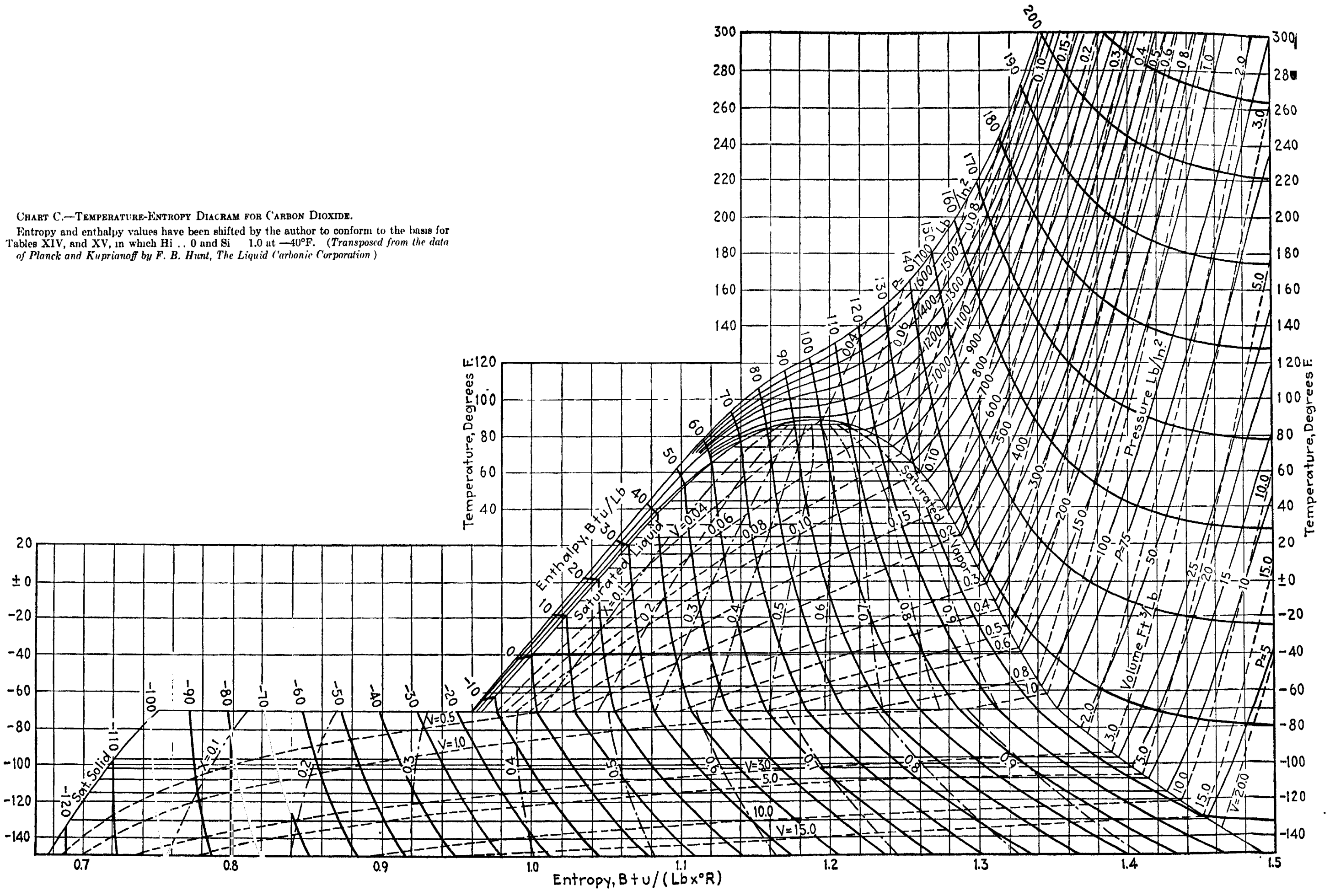
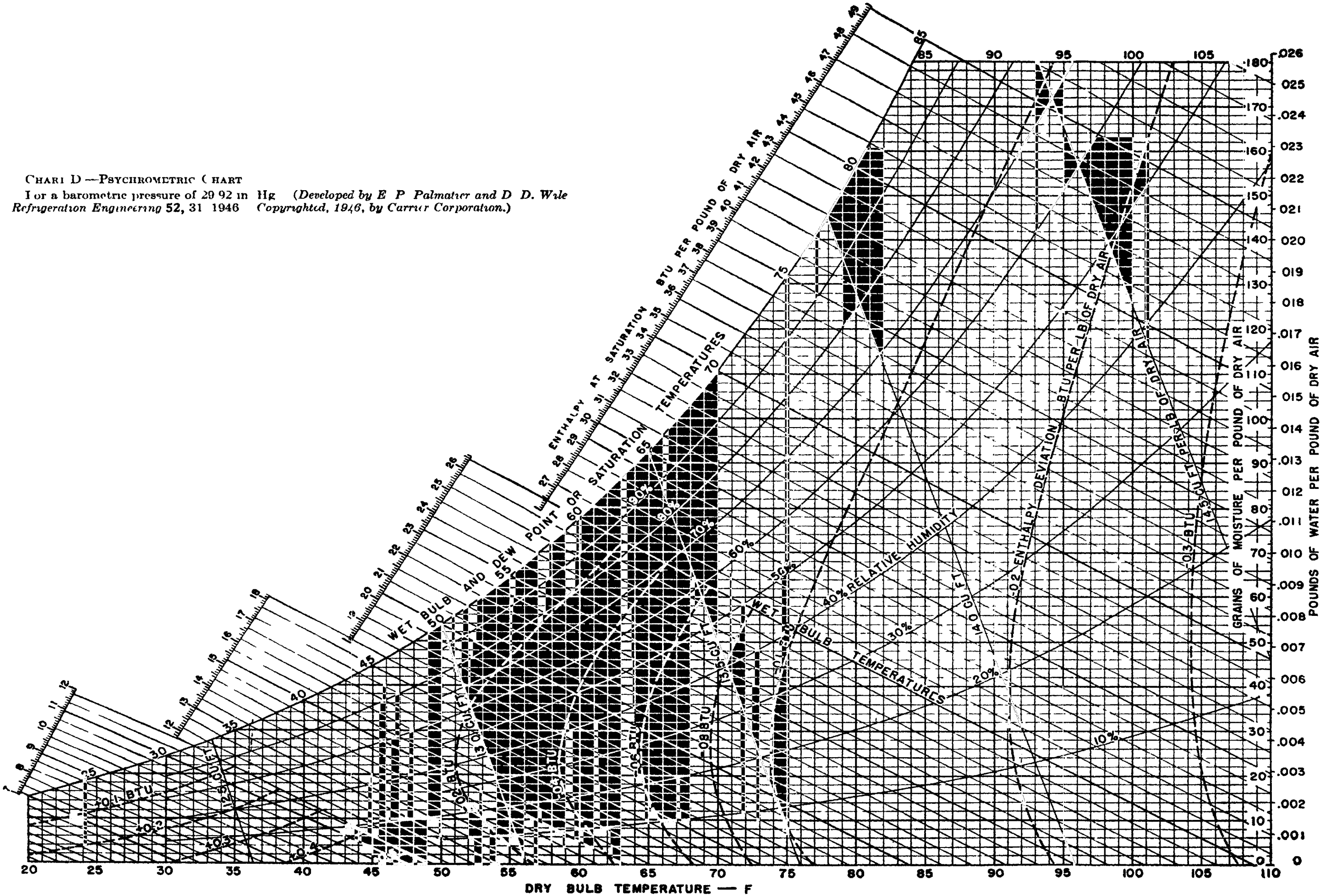


CHART C.—TEMPERATURE-ENTROPY DIAGRAM FOR CARBON DIOXIDE.

Entropy and enthalpy values have been shifted by the author to conform to the basis for Tables XIV, and XV, in which H_i .. 0 and S_i 1.0 at —40°F. (*Transposed from the data of Planck and Kuprianoff by F. B. Hunt, The Liquid Carbonic Corporation.*)

CHART D.—PSYCHROMETRIC CHART

For a barometric pressure of 29.92 in. Hg. (*Developed by E. P. Palmatier and D. D. Wile. Refrigeration Engineering* 52, 31. 1946. *Copyrighted, 1946, by Carrier Corporation.*)



BELOW 32°F PROPERTIES ARE FOR ICE.

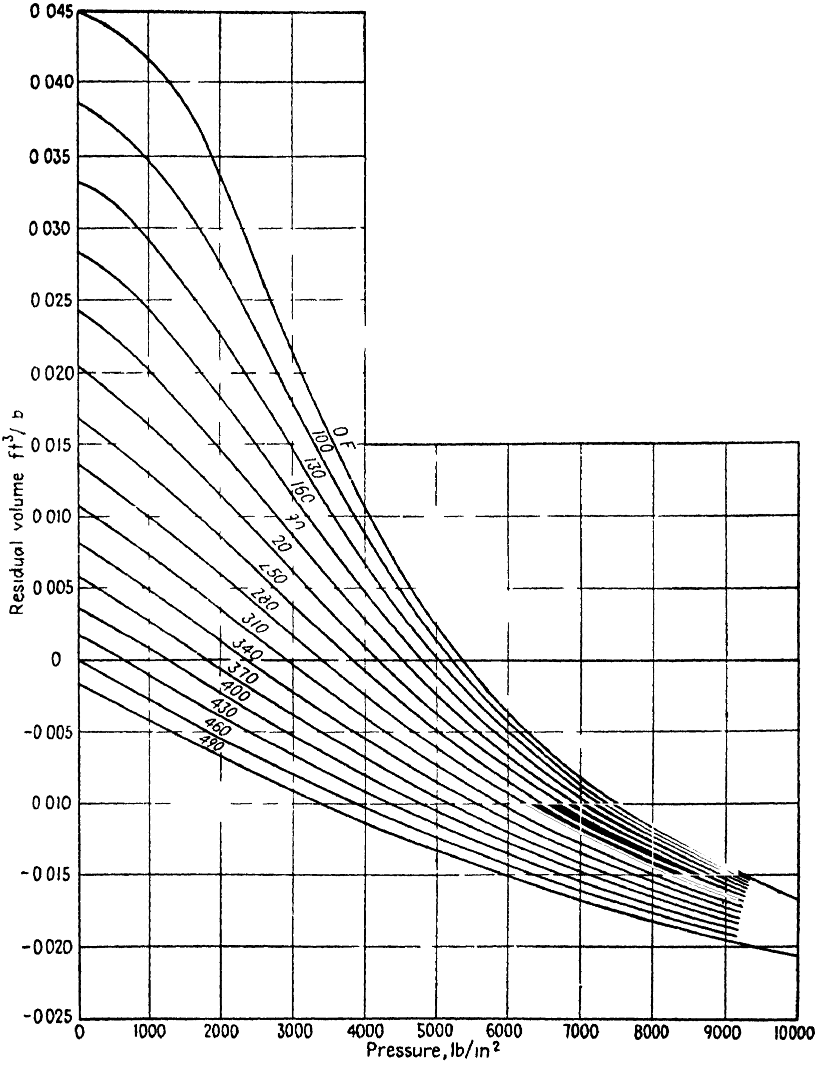


CHART F — RESIDUAL SPECIFIC VOLUME OF METHANE (*R H Olds H H. Reamer B H Sage and W N Lacey Volumetric Behavior of Methane Ind & Eng Chem* **35,** 922, 1943)

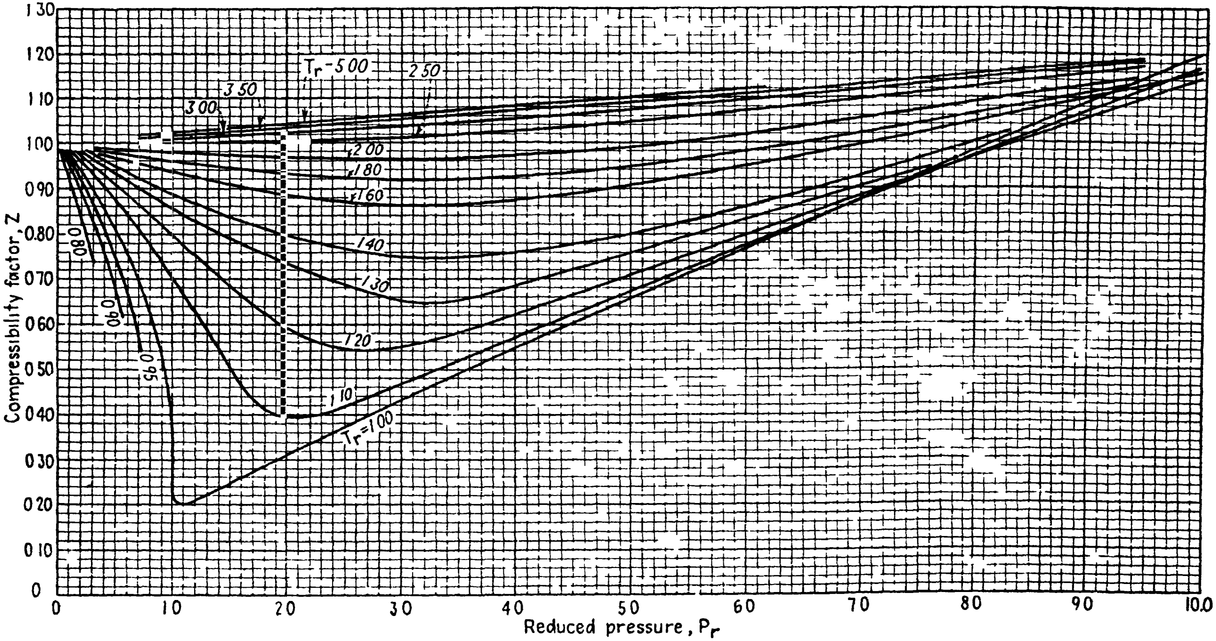


Chart F.—Compressibility Factor Versus Reduced Pressure for Various Reduced Temperatures. Low-pressure range. (B. F. Dodge, *Chemical Engineering Thermodynamics*, McGraw-Hill Book Company, Inc., New York, 1944.)

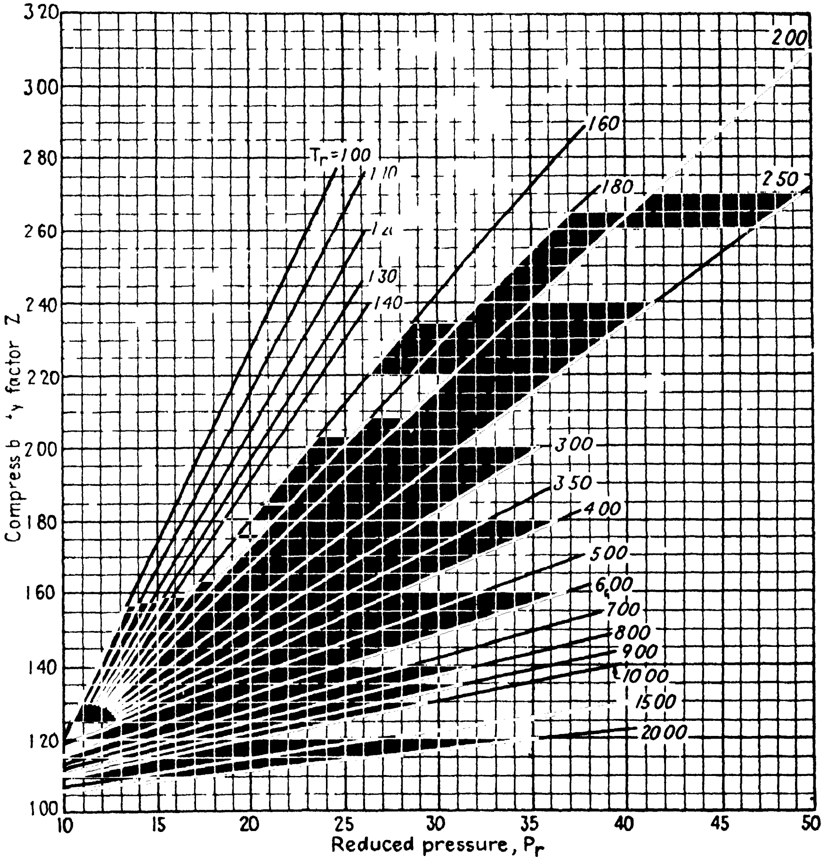


CHART G. COMPRESSIBILITY FACTOR VERSUS REDUCED PRESSURE FOR VARIOUS REDUCED TEMPERATURES. High pressure range. (*B. F. Dodge, Chemical Engineering Thermodynamics, McGraw-Hill Book Company, Inc., New York, 1944.*)

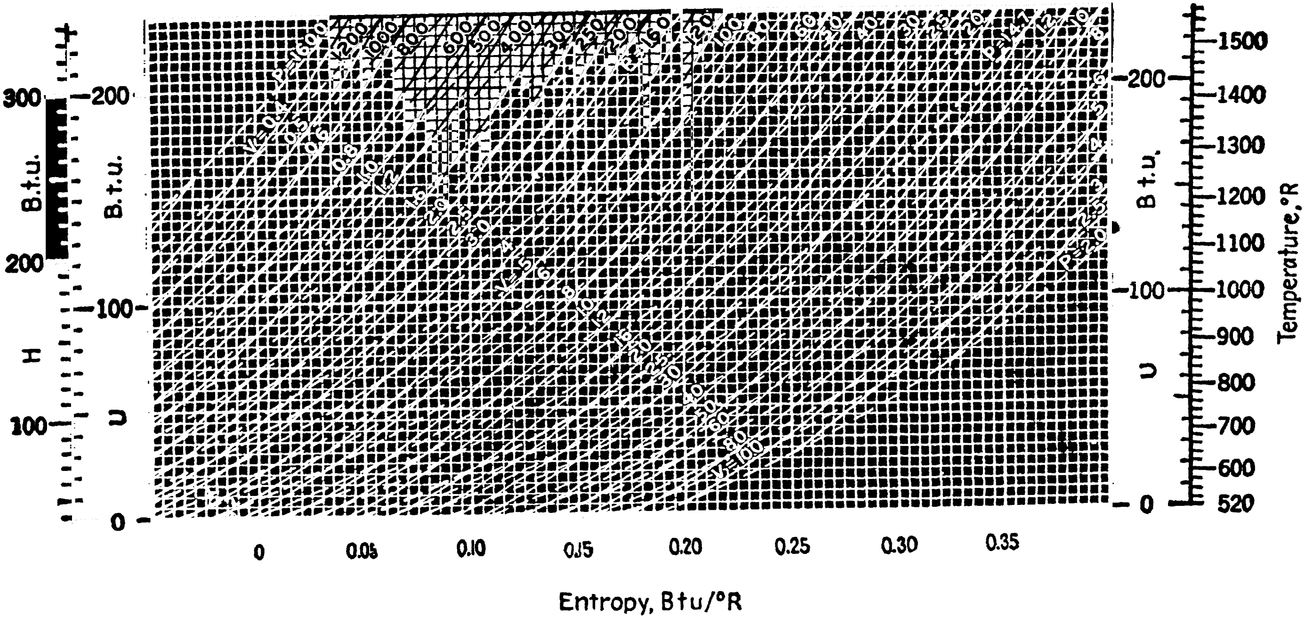


Chart H.—Energy-Entropy Diagram of Correct Mixture of Octane and Air and Clearance Gases. C = 1278 (1—f). This chart is based on a clearance gas fraction of 0.10. (*R. L. Hersey, J. E. Eberhardt, and H. C. Hottel, Thermodynamic Properties of the Working Fluid in Internal Combustion Engines, S.A.E., Trans.*, **31**, 409, 1906.)

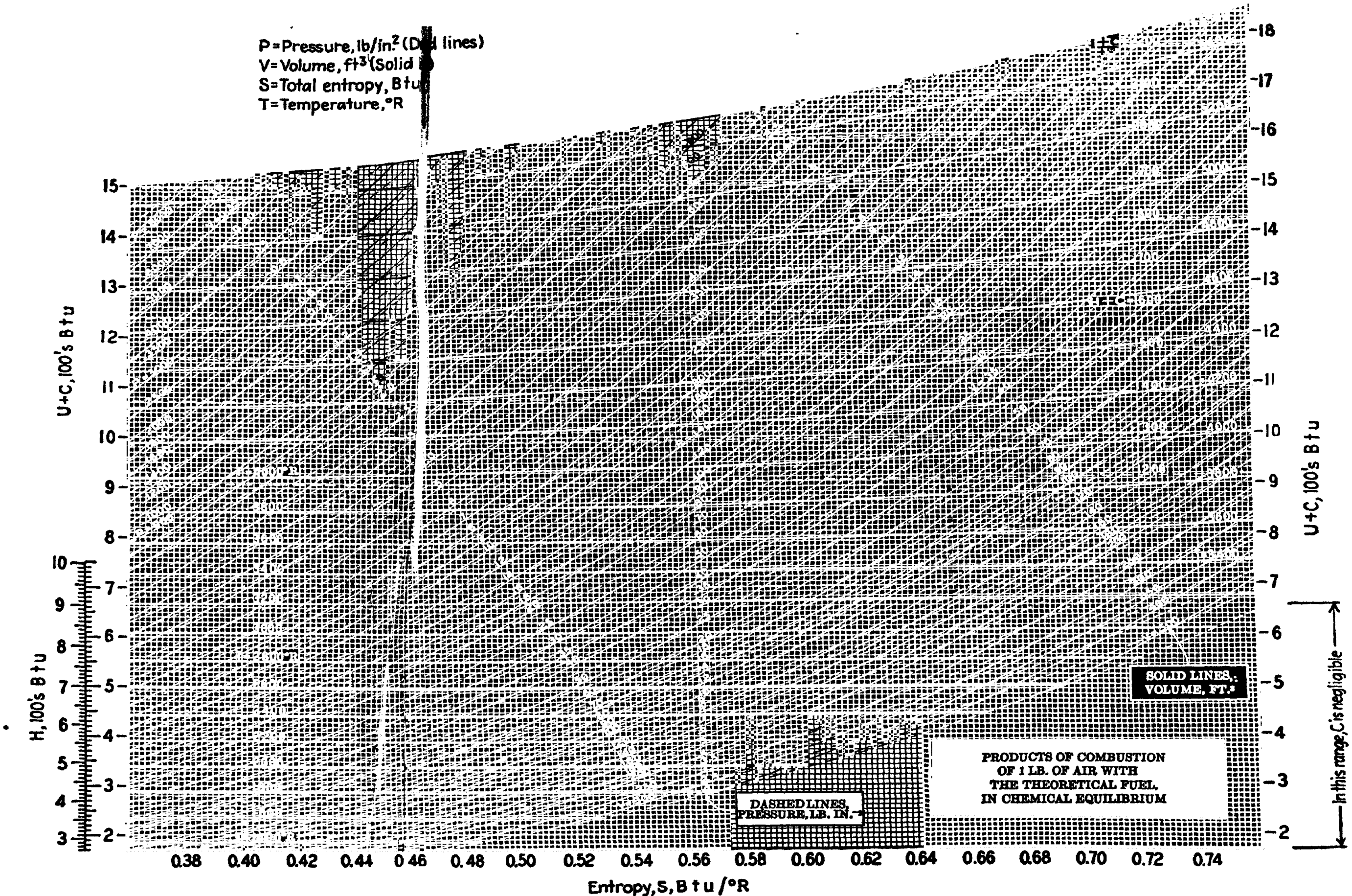
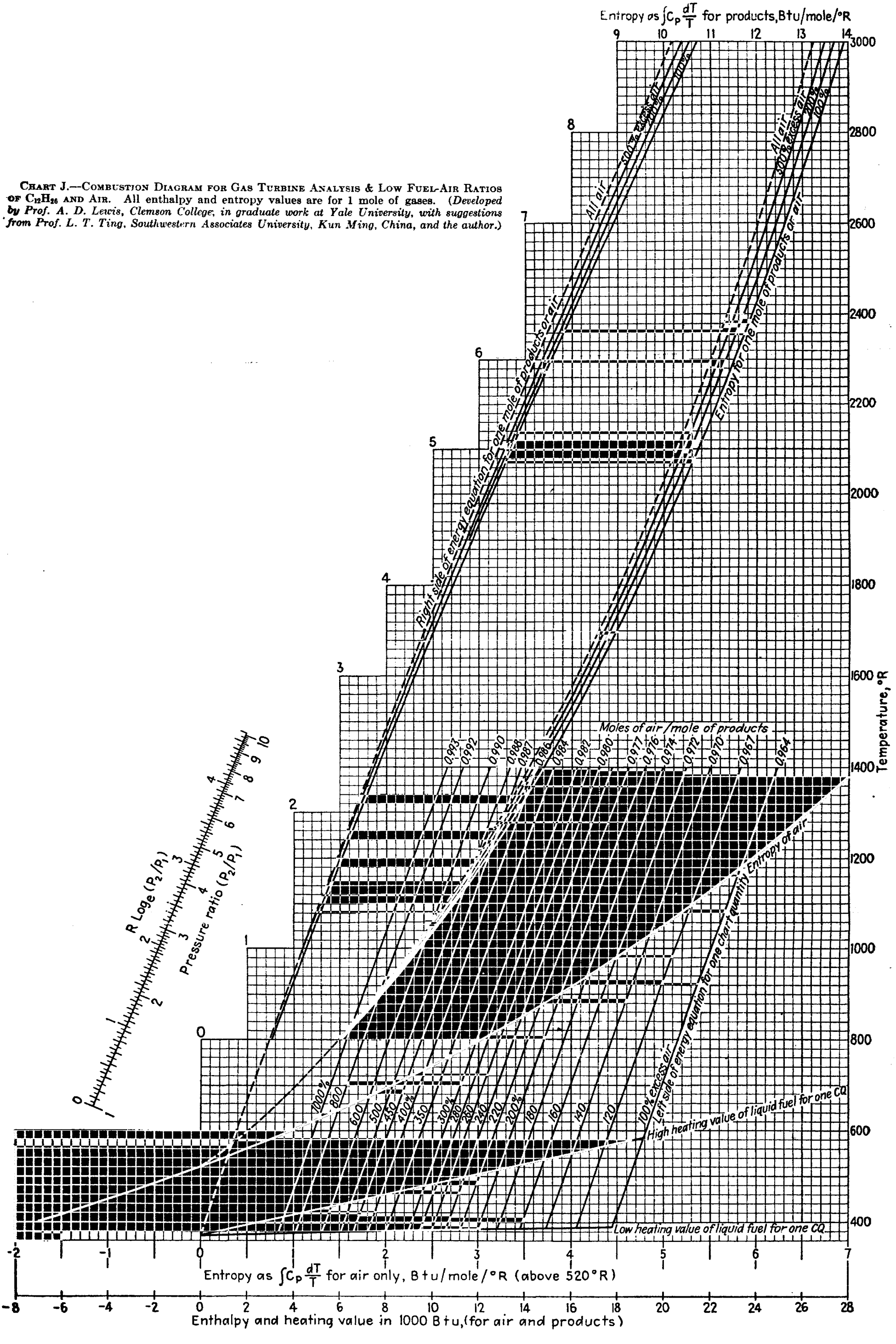


Chart I.—Energy-Entropy Diagram for Products of Combustion of Correct Mixture of Octane and Air. (15.11 to 1 air-fuel ratio.) Before combustion C = 1278 (1—f). (*Based upon data of R. L. Hersey, J. E. Eberhardt and H. C. Hottel, Thermodynamic Properties of the Working Fluid in Internal Combustion Engines, S.A.E. Trans.*, **31**, 409, 1936.)

CHART J.—COMBUSTION DIAGRAM FOR GAS TURBINE ANALYSIS & LOW FUEL-AIR RATIOS OF $C_{12}H_{26}$ AND AIR. All enthalpy and entropy values are for 1 mole of gases. (*Developed by Prof. A. D. Lewis, Clemson College, in graduate work at Yale University, with suggestions from Prof. L. T. Ting, Southwestern Associates University, Kun Ming, China, and the author.*)



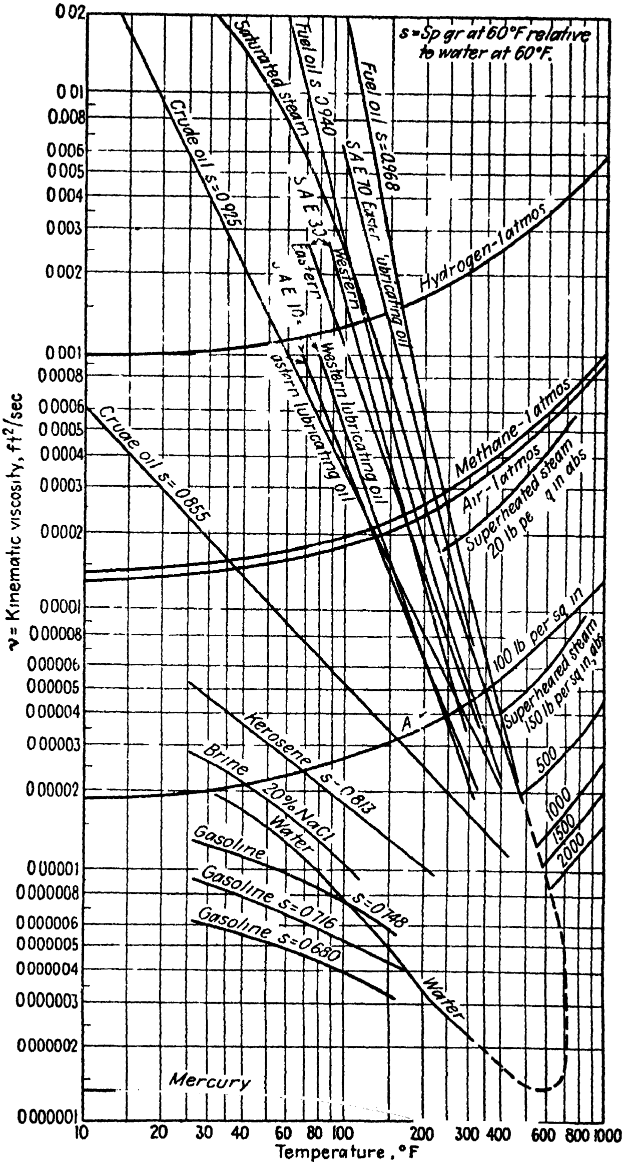


Chart K —Kinematic Viscosity of Various Fluids (*Daugherty, R L, "Hydraulics," 4th ed, McGraw-Hill Book Company, Inc, New York, 1937*)

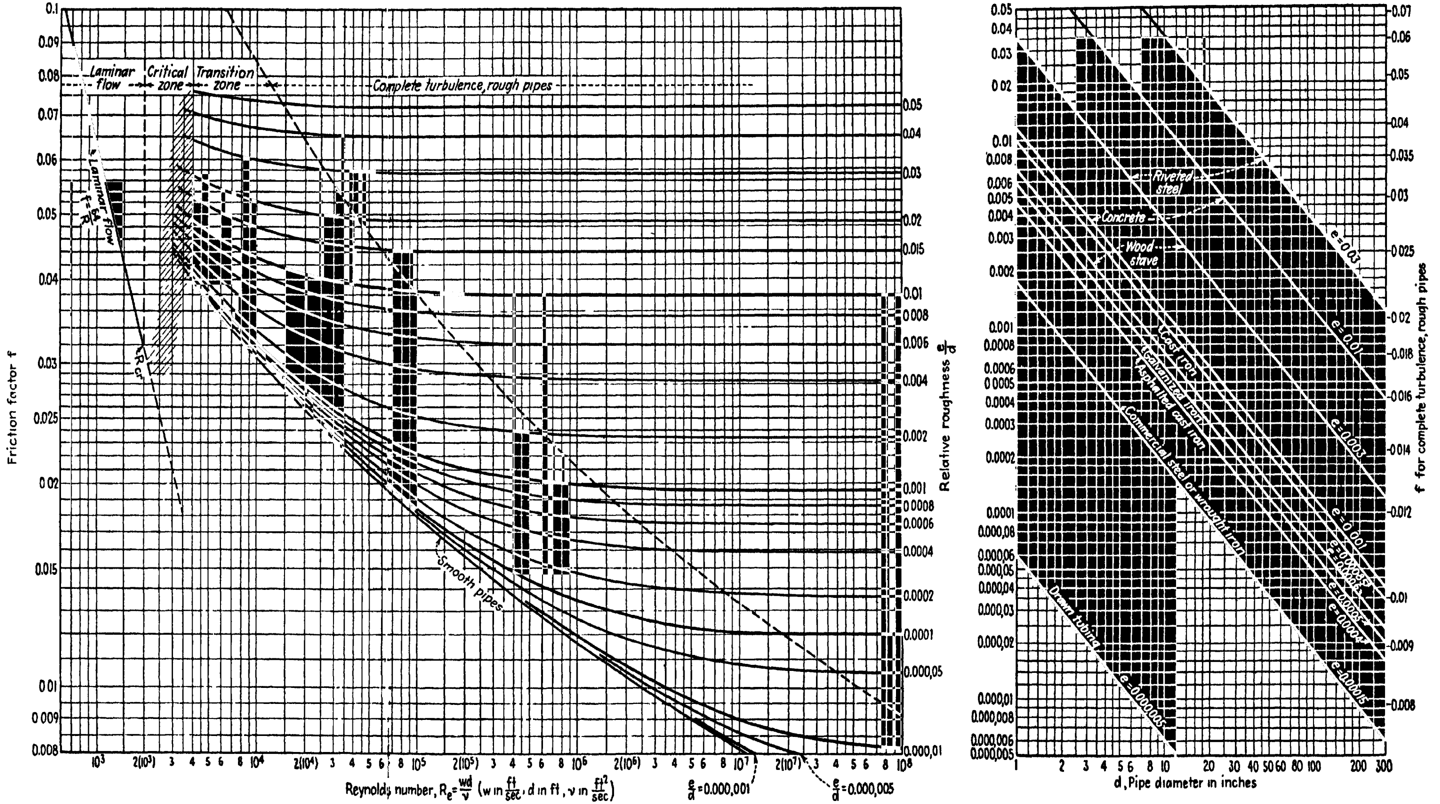


CHART I.—FRICTION FACTORS FOR PIPE-LINE FLOW. (*Moody, Lewis E., Friction Factors for Pipe Flow, A.S.M.E. Jour., Nov., 1944, p. 671.*)

(*G. F. Wislicenus*)